PB85-174803

Experimental Study of Lake Loading by Aerosol Transport and Dry Deposition in the Lake Erie Basin

Governors State Univ., University Park, IL

Prepared for

Environmental Protection Agency, Chicago, IL

Jun 84

U.S. Department of Commerce
National Technical Information Service
NTIS

United States
Environmental Protection
Agency

Great Lakes National
Program Office
536 South Clark Stree
Chicago, Illinois 60605

EPA-905/2-84-002

PB85-174803

EPA

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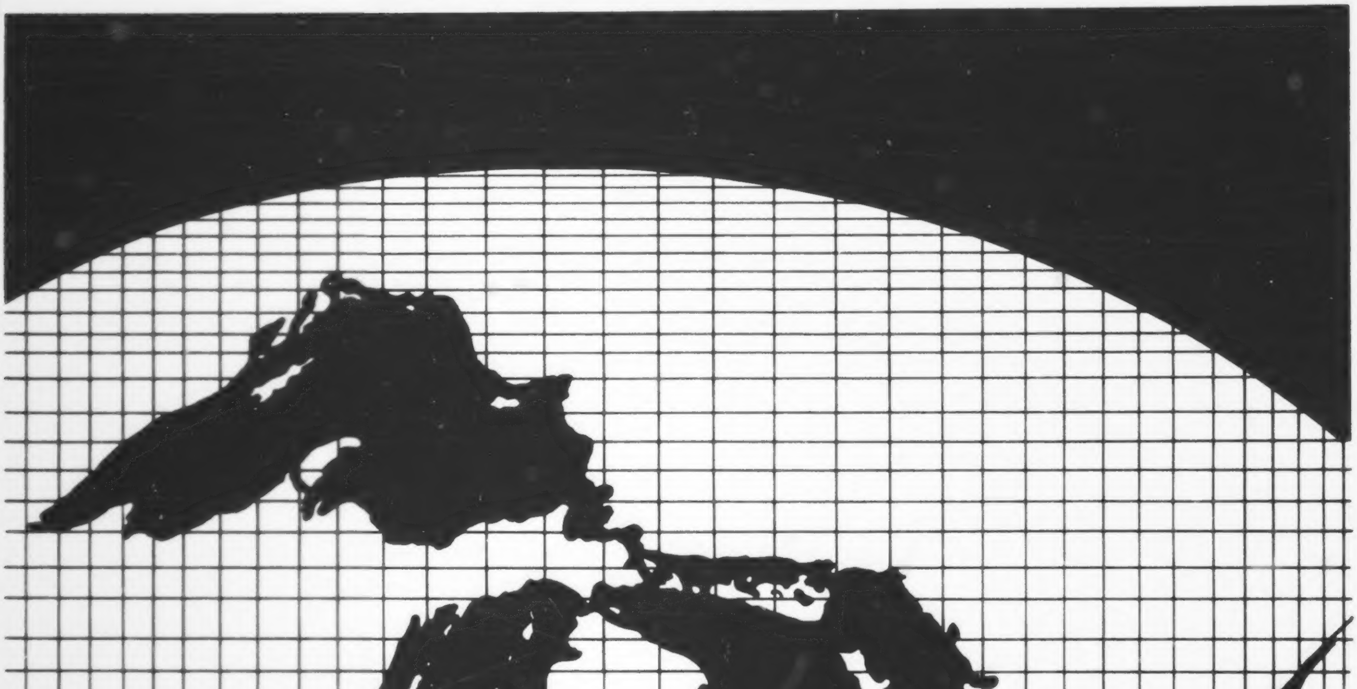

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(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-905/2-84-002	2.	3. RECIPIENT'S ACCESSION NO. PB85 174803/AS
4. TITLE AND SUBTITLE An Experimental Study of Lake Loading By Aerosol Transport and Dry Deposition in the Lake Erie Basin		5. REPORT DATE June 1984
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) H. Sievering, D. A. Dolske, V. Jensen and R. L. Huges		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Governors State University University Park, Illinois 60466		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO. R00530101 R00542101
12. SPONSORING AGENCY NAME AND ADDRESS U. S. Environmental Protection Agency Great Lakes National Program Office 536 South Clark Street, Room 958 Chicago, Illinois 60605		13. TYPE OF REPORT AND PERIOD COVERED Research 1979
		14. SPONSORING AGENCY CODE Great Lakes National Program Office, U.S. EPA, Region V
15. SUPPLEMENTARY NOTES Ed Klappenbach Project Officer		

16. ABSTRACT

The purpose of this study of Lake Erie was to obtain an over lake data base and to relate aerosol chemical constituent loadings. Information collected at each scale is necessary to expand our understanding of the complex aerosol transport and deposition process that occur over the lake.

It is believed these results obtained from the Great Lakes Atmospheric Deposition(GLAD) network, should lead to a more generalized understanding of aerosol transport and deposition in the Great Lakes region, as well as a better estimation of atmospheric-route Great Lakes Pollution loading.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field Group
Dry loading Wet loading Aerosol transport Chemical analysis Monitoring Air pollutants Site sampling		

18. DISTRIBUTION STATEMENT Document is available to the public through the National Technical Information Service (NTIS), Springfield, VA 22161	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES 168
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (9-73)

EPA-905/2-84-002
June 1984

AN EXPERIMENTAL STUDY OF LAKE LOADING BY AEROSOL TRANSPORT AND DRY DEPOSITION IN THE LAKE ERIE BASIN

by

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FOREWORD

This study was supported by a Great Lakes National Program grant to Governors State University for investigating the rate of deposition of atmospheric transported pollutants to Lake Erie. The R/V Carson, a laboratory and lake water quality sampling ship, operated by this office, was used to support this project. Data in this report covers a period from June 1979 to July 1982.

DISCLAIMER

This report has been reviewed by the Great Lakes National Program Office, Region V, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

EXECUTIVE SUMMARY

A Lake Erie experimental program to assess the contribution of atmospheric dry loading of aerosol trace elements and nutrients has been completed. Trace elemental concentrations were determined by atomic emission spectroscopy for seventeen elements. Nutrient species phosphate and sulfate were determined by standard USEPA techniques.

The Lake Erie sampling program was successful, despite generally poor weather conditions. However, any attempt to calculate atmospheric dry loading must be viewed with skepticism. The very fact that unusual weather conditions prevailed during at least two of the three Lake Erie ship outings means that the data base is not climatologically representative. Neither the aerosol elemental concentrations nor the wind speed and direction data are sufficiently representative to allow use of the Lake Michigan "binning" procedure (EPA-905/4-79-016). For example, no high wind speeds (i.e., greater than 10 m s^{-1}) or thermally unstable conditions were encountered. Southwesterly flow from the Cleveland source region was severely under-represented. Also confounding, though, is the fact that rains (often times heavy) and, therefore, wet soil/surface conditions prevailed during the Lake Erie sampling program. These conditions caused the aerosol concentrations for soil-derived elements (e.g., Iron) to be more than one order-of-magnitude lower over Lake Erie than over Lake Michigan. These "rainy" conditions must also have affected anthropogenic source elemental (Pb, Zn, Cd, Cu, Cr, Ni--see Table next page for explanation of symbols) concentrations. Yet the observed Zn, Cd, Cu, Cr, and Ni ambient air concentrations are comparable to previous measurements in the northeastern U.S. This, and the fact that Zn, Cd, Cu, Cr, and Ni are suspected to be near to toxic levels in Lake Erie waters, provoked the calculation of atmospheric loadings below--presented in metric tons per year (10^3 kg yr^{-1}). Results are shown along with revised estimates for the southern basin of Lake Michigan (EPA-905/4-79-016).

The range in values shown may be considered to be the $\sim$25% and $\sim$75% confidence limits in the estimation of mean loadings. The full range of uncertainty may be more than an order of magnitude. Thus, these loading numbers must be "viewed with skepticism" as stated above.

ATMOSPHERIC DRY LOADING, 10^3 kg yr^{-1}

Element		Lake Erie	Southern Basin Lake Michigan	Percentage Anthropogenic	
				Lake Erie	Lake Michigan
Iron	(Fe)	170-330**	350-850	>75	>65
Lead	(Pb)	10-25	200-500	>95	95
Zinc	(Zn)	120-300	70-200	>97	>75
Cadmium	(Cd)	8-20	---	>99	--
Copper	(Cu)	15-50	(10-20)*	$\sim$95	(?)*
Chromium	(Cr)	8-18	---	>80	--
Nickel	(Ni)	5-15	---	$\sim$90	--
Sulfate	$(SO_4^=)$	$20\text{-}50 \times 10^3$	$3.5\text{-}11 \times 10^3$	--	--
Phosphorus (Total-P)		< 10**	75-150	--	--

---

[*] Parens indicate dubious nature of Lake Michigan Cu data because of sampling contamination.

[**] Low due to depleted soil source during Lake Erie sampling program.

A first point to notice is that numbers for Cd, Cu, Cr, and Ni are available for Lake Erie but not for Lake Michigan. This is the result of improved analytical detection limits as well as the fact that average sampling times over Lake Erie were nearly twice as long as over Lake Michigan. The Fe and total-P Lake Erie loadings are three- to ten-fold lower than for Lake Michigan because of the markedly depleted soil source.

These two loading figures are certainly unrepresentatively low estimates. The Pb, Cr, and Ni loading estimates may also be unrepresentatively low. (A previous Lake Erie dry loading estimate [IJC, 1977] for Pb is 600×10^3 kg yr^{-1}; this value may be an over-estimate.) Clearly Pb loading, primarily from automotive and other combustion sources, is reduced relative to that for the southern basin of Lake Michigan, even considering the order-of-magnitude potential uncertainty. In light of this, the estimated Zn loading to Lake Erie is surprisingly large. Considering the large uncertainty prevalent, the atmospheric dry loading of Zn to Lake Erie and to the southern basin of Lake Michigan are about the same. In the case of Lake Michigan, atmospheric Zn dry loading constitutes about one-third of the total loading from dry and wet deposition and from runoff combined.

One may calculate the relative contribution of the soil- and lake-derived natural aerosol sources versus anthropogenic aerosol sources, on the assumption that all sources other than soil and lakes are anthropogenic. Results of this calculation are shown in the last two columns of the table. Since the percentage of anthropogenic Pb, Cd, and Cu is comparable to that for Zn, it is suggested that a substantial percentage--at least 10% to as much as 50%--of the total Lake Erie loading for these elements may be due to dry deposition. However, before any comparisons with wet deposition and runoff are considered valid, a larger Lake Erie aerosol data base must be obtained. For Zn and Cu alone it is estimated that 30 to 50% of their atmospheric dry loading may occur during high wind speeds (i.e., greater than 10 m s^{-1}). Yet no data were obtained during such conditions nor during thermally unstable conditions (which prevail in winter months). It is also impossible to use the combined Lakes Erie and Michigan data base to further estimate loadings for others of the Great Lakes.

Given the difficulty in obtaining loading estimates for Lake Erie a second look at the Lake Michigan data base was undertaken. In particular, the chemical element balance (CEB) approach was used to evaluate the percentage contribution to over-Lake Michigan aerosol mass by each of seven source types: the lake itself, soil, surface excavation (e.g., rock quarrying), iron/steel manufacturing, residential oil-burning, coal-burning and automobile combustion. It was found that the lake may be a large contributor to the total aerosol mass observed overlake although neither of the natural lake or soil sources is a major contributor to the trace elements Cd, Pb, or Zn mentioned above.

The final area of research during this Lake Erie Grant program was an effort to better parameterize aerosol deposition at the air/water interface. During the Lake Michigan Grant program a simple estimate of the deposition velocity (v_d) at the air/water interface was made by assuming it to be a product of wind speed and the drag coefficient. One way to obtain a better parameterization is by estimating v_d as a function of smooth, moderate, and rough flow conditions at the air/water interface. Consideration of these three distinct flow regimes results in an average v_d about half the value previously used. As a consequence, the range in previously reported Lake Michigan loading values is nearly one-half of that reported in EPA-905/4-79-016 . This approximately twofold reduction is reflected in the Lake Michigan southern basin loadings shown in the table in this Executive Summary.

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SECTION 1

INTRODUCTION

The U.S.-Canada Agreement on the Great Lakes has, in the past few years, stimulated research into the relationship between regional air pollution and the lakes' water quality. A part of the USEPA effort in this regard has been grant funding, through the Great Lakes National Program Office (GLNPO), of studies addressing various aspects of atmospheric-route loading. Projected future shoreline and inland population gains, industrial development, and energy producing facilities make the atmospheric route a critically important element in the overall problem of Great Lakes pollution loading. The region encompasses several intense urban-industrial air pollution source areas. Prevailing winds often carry anthropogenic particles and gases out over the lakes. A real potential exists for serious detrimental effects on Great Lakes water quality.

In order to achieve accurate estimates of atmospheric-route loadings, the processes of wet and dry deposition are probably best considered separately. Bulk (wet plus dry) sampling presently gives no better than an order-of-magnitude accuracy in the dry loading estimation. Regarding small particles (the vast majority of anthropogenic particles are small particles), sampling techniques that simulate natural-surface particle collection efficiency do not yet exist. Wet deposition loadings have been reliably known for years. And, dry deposition loadings had been considered negligible until early modelling estimates suggested dry loadings could be substantial (Winchester and Nifong, 1971; Gatz, 1975; Sievering, 1975). A lack of knowledge regarding temporal variability in ambient aerosol concentration and deposition rate pointed out the need for environmental (field) sampling as a means of decreasing the uncertainty in estimates of the dry deposition loading rate. During a 1976-1979 study by Governors State University (GSU) aerosol and meteoological data were collected over mid-Lake Michigan (Sievering et al., 1979). Aerosol concentrations and deposition rates were found to be strongly dependent on surface layer meteorological conditions. The uncertainty in estimates of dry deposition loadings for Lake Michigan was reduced; however, the applicability of the conclusions of that study to the other Great Lakes remained in question. This present work was funded in 1979 by USEPA-GLNPO, to complement and extend the results of the earlier Lake Michigan work by GSU. A sampling program using identical or compatible methods was carried out during the summer of 1979 on Lake Erie. Ultimately, the conclusions of this work, in conjunction with Lake Michigan results and those obtained from the Great Lakes Atmospheric Deposition (GLAD) network, should lead to a more generalized understanding of aerosol transport and deposition in the Great Lakes region, as well as a better estimation of atmospheric-route Great Lakes pollution loading.

The principal objectives of the present work on Lake Erie were to obtain an overlake data base and to relate aerosol chemical constituent loadings to climatologically-expected meteorological conditions over Lake Erie. In order to approach these objectives, a data collection program was devised that covered a wide range of spatial and temporal scales--see Figure 1. Aerosol monitoring, at the smallest space scales, included Active Scattering Aerosol Spectrometer (ASAS) aerosol number concentrations, condensation nuclei counter (CNC) number concentrations, and integrating nephelometer (IN) back scattering coefficient. Hi-volume samplers collected particles during filter exposures which averaged about six hours. Cascase impactors and several types of filter material were used to provide appropriate media for the several chemical analyses that were done. A separate pass-through experiment using hi-volume air sampling at GSU and the 68th Street Crib near Chicago was performed during 1980 in order to determine the percentage of Pb, Zn, and Fe lost (passed through) by hi-volume filter sampling. Results of the pass-through experiment (PTE) are used to correct trace metal concentration data obtained during Lake Erie hi-volume air sampling and, also, Lake Michigan sampling.

A second major data collection thrust was meteorological in character. Micrometeorological information was collected and processed by GSU. Larger space- and time-scale meteorological data were obtained

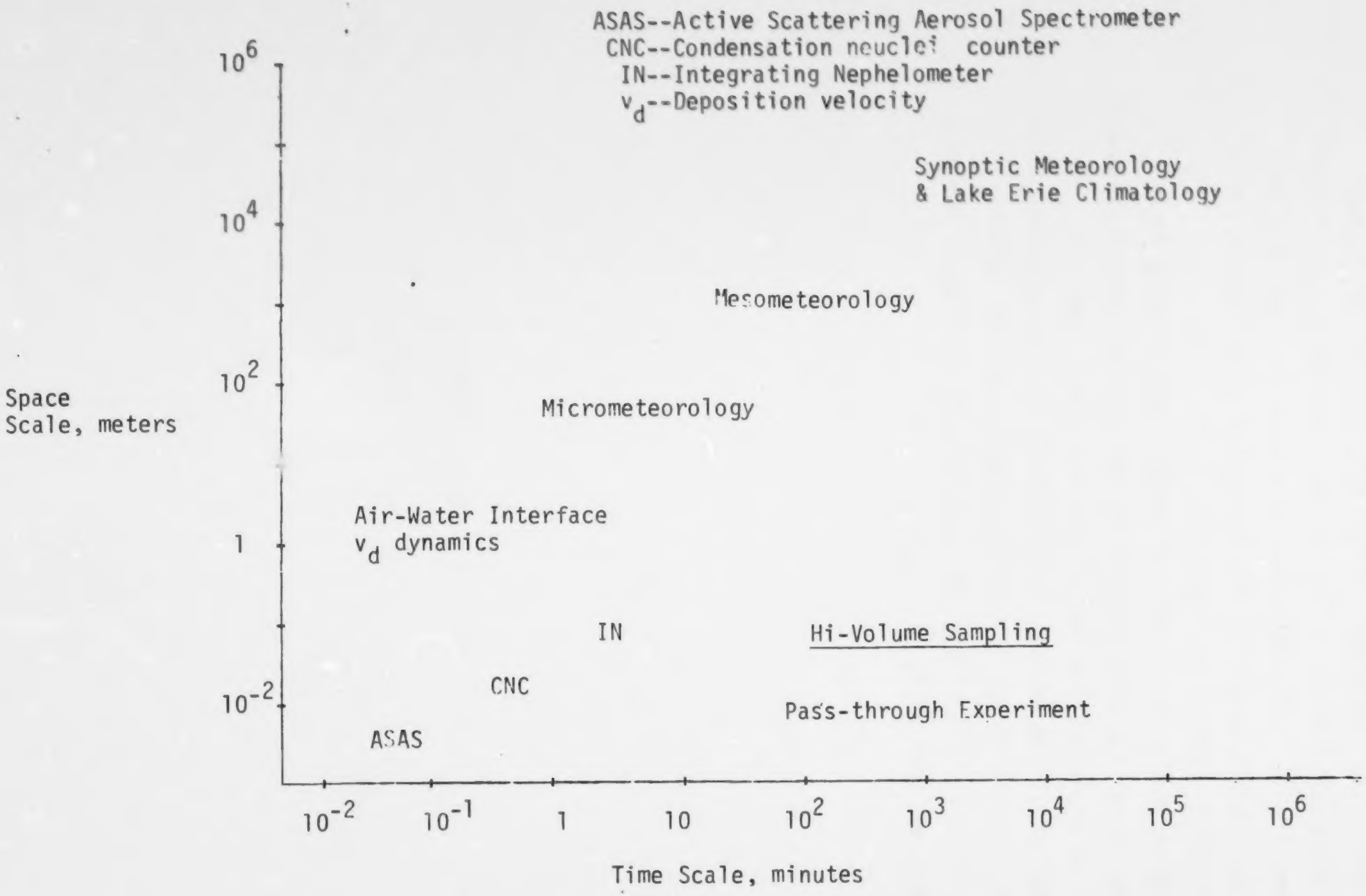


Figure 1. Data Collection areas for GALE, 1979-1980.

from the U.S. Coast Guard (USCG) and National Weather Service (NWS) stations around the lake, Canada Centre for Inland Waters (CCIW) Lake Erie buoys, and Atmospheric Environment Service (AES) shore stations. Correction and reduction of the raw meteorological data was performed at GSU. Climatological data were obtained from the National Oceanic and Atmospheric Administration (NOAA Summary of Synoptic Meteorol. Obser. for Great Lakes Areas, 1975).

Information collected at each of these scales (Figure 1) is necessary to expand our understanding of the complex aerosol transport and deposition processes that occur over the lake. Chemical characterization of the aerosol, construction of backtrajectory plots, calculation of estimated deposition velocities, and the relation of those factors to Lake Erie climatological data ultimately approach the objectives of this study.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The loading of Great Lakes' waters by air pollutants is an extremely difficult process to thoroughly understand on qualitative grounds let alone to establish quantitatively. Yet, a number of conclusions can be drawn from this Lake Erie study:

1. Single point (shipboard) over lake sampling can be made to be representative of an entire Great Lake's meteorological conditions to better than ± 15% accuracy.
2. Insufficient aerosol elemental and compound data were obtained over Lake Erie to afford the detailed calculation of loading estimates by the procedure used in the Lake Michigan study (EPA-905/4-79-016). However, rough estimates of Cu, Zn, Cd, Cr, and Ni loadings are warranted given their potential for negative ecological impact.
3. Extrapolation and interpolation of Lake Michigan or Lake Erie aerosol elemental concentrations to others of the Great Lakes is not warranted. Long-range aerosol transport may well have markedly changed the absolute as well as relative concentrations of trace elements over Lake Erie. It would be better to monitor the anthropogenic contribution to Great Lakes' loading at a site not dominated by long-range transport that is, yet, representative of overlake conditions on the Great Lakes. These conditions were met at the midlake site on southern Lake Michigan but not by the mid-Lake Erie nor the Lake Michigan nearshore (water intake crib) site sampling.
4. In light of 3, the Lake Michigan data have been reconsidered to review lake effects upon aerosol transport and, especially, trace element concentrations. This reconsideration of Lake Michigan concentrations has also included the determination of aerosol losses in the sampling apparatus used over Lake Michigan to then arrive at revised atmospheric dry loading estimates for Lake Michigan.

5. Anthropogenic, soil and lake source contributions to over Lake Michigan aerosol concentrations have been preliminarily specified by using a chemical element balance technique. Results indicate an unexpectedly large lake source contribution to the total aerosol mass. This was found to be true for both fine and coarse aerosol particulate matter. However, the contribution of steel manufacturing and surface mining industries and of coal burning and the automobile were by no means insignificant. In fact, anthropogenic contributions (in parens)--at the Lake Michigan nearshore site were found to be: Pb (99%), Zn (95%), and Mn (90%). It would appear that an intensive aerosol sampling, multi-element analysis and, especially, a multivariate statistical interpretation (including uncertainty)--in concert with a detailed meteorological/climatological assessment--may best ultimately unravel anthropogenic versus natural loadings. More important, anthropogenic contributions by source type to overlake aerosol concentrations (with $\leq$ 50% uncertainty) may result.
6. The accurate determination of loadings to any of the Great Lakes must await a reasonably accurate parameterization of aerosol deposition velocities (v_d) as a function of aerosol particle size (or chemical element), of wind speed and direction, of thermal stability and of temporal or spatial changes in these parameters. Our understanding of over-water v_d dependence on these parameters is extremely limited and warrants the consideration of research specifically designed to determine these dependencies.

SECTION 3
DESCRIPTION OF EXPERIMENTAL PROGRAM

3.1 THEORY AND DESIGN

In order to illustrate the basic concepts and data-collection requirements of the experiment, the simple relation

$$F = v_d \cdot C \tag{1}$$

may be used. F is the mass flux of particles to the lake surface (kg m^{-2} s^{-1}), v_d is the deposition velocity (m s^{-1}), and C is the concentration (kg m^{-3}) of particles in air near the surface. Note that both v_d and C are complicated functions of many environmental factors, as discussed further in this report. However, equation 1 does show that there are two main areas to investigate when estimating F.

Particle and interface physics and micrometeorological factors enter into the determination of v_d; aerosol chemical transformations and the mechanics of particle transport downwind of source regions affect the determination of C. Finally, the climatological record is used to normalize the temporal variability in F to expected mean annual conditions, yielding annual total dry deposition loading estimates. Overlake climatology is thus an important factor in the determination of annual loading rates (see Section 5.1). In order to relate the limited number of sampling hours (approximately two percent of the year) to the annual total loading, data sets taken in periods of similar surface layer conditions are computationally grouped into "bins." Each bin is defined by a range of values for one of three parameters: thermal stability, wind speed and source region, the last identified through back-trajectory analysis. For each of the j bins the annual frequency of occurrence, f_0, is determined for the range of the defining parameters. The climatological dependence of v_d and C are then calculated from: the NOAA Summary of Synoptic Meteorological Observations for Great Lakes Areas (NOAA, 1975).

$$\text{Annual Dry Loading} = \sum_j \bar{v}_{dj} \cdot \bar{C}_j \cdot f_{oj} \cdot A \cdot \frac{t}{\sum_j f_{oj}} \qquad (2)$$

where: $\bar{v}_{dj}$ is the mean v_d for aerosol data sets in the jth bin ($m\ s^{-1}$); aerosol (chemical constituent)

$\bar{C}_j$ is the mean aerosol (chemical constituent) concentration for data sets in the jth bin ($kg\ m^{-3}$);

f_{oj} is the annual frequency of occurrence for the defining range of the three parameters--thermal stability, wind speed and source region;

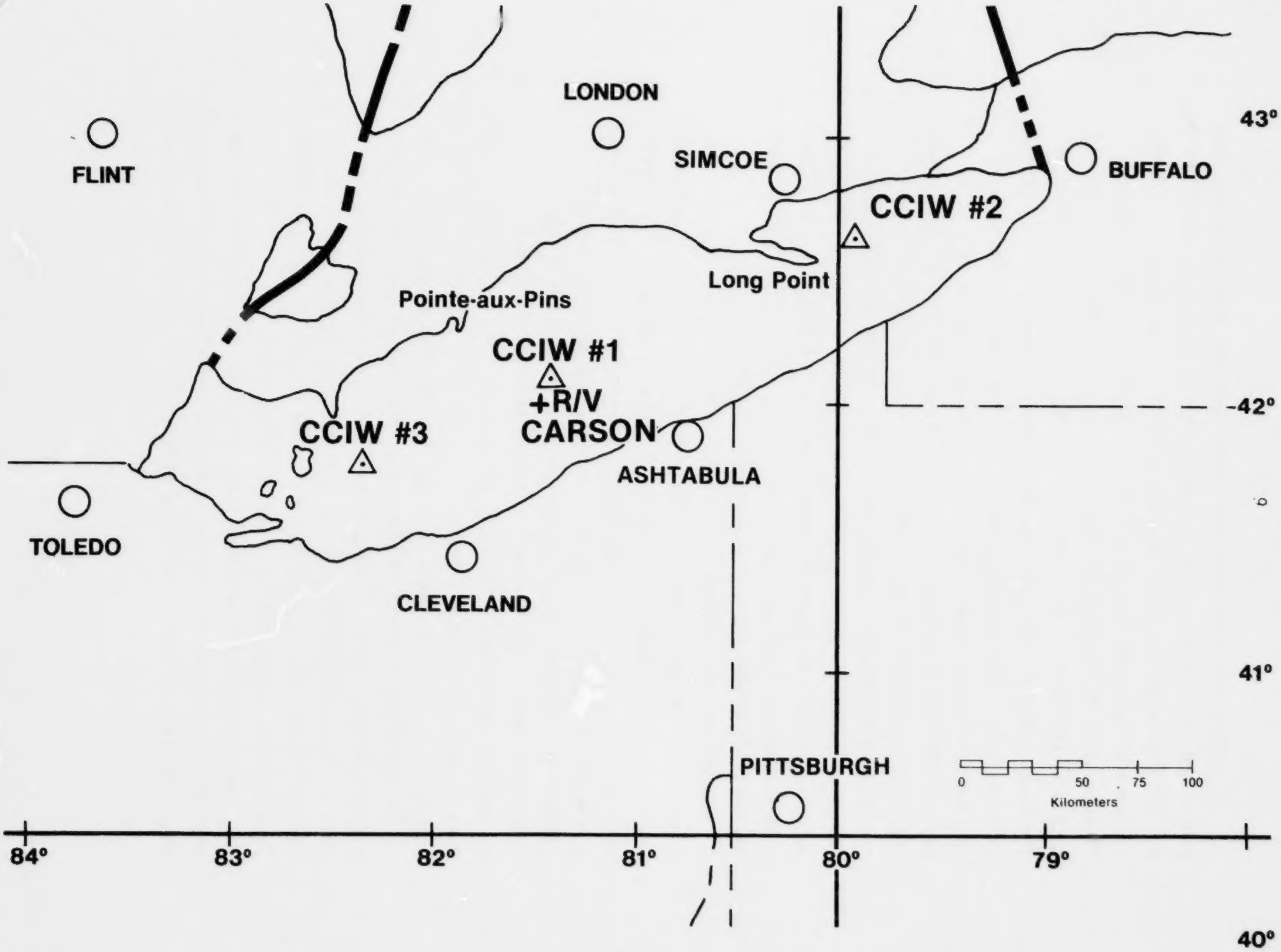
A is the total water surface area of the Lake Erie basin (m^2);

and t is that part of the year when no precipitation occurs overlake ($s\ yr^{-1}$).

Further discussion of basic concepts of the experimental program may be found in the final report of the 1976-1979 Lake Michigan study (Sievering et al., 1979).

Meteorological data were collected from several U.S. and Canadian shoreline stations and buoys in Lake Erie. These data were used extensively in the construction of aerosol back-trajectories, by the methods of Sievering et al. (1979). In conjunction with climatological information (NOAA, 1975), an attempt was made to estimate the representativeness of the year 1979 and the limited sampling periods. The meteorological data used were: Canadian climatological station data for Long Point and Port Colborne, Ontario; Canadian surface data for London and Dimcoe, Ontario; three Lake Erie CCIW buoy locations: Buoy #1 (42° 07' 42" N, 81° 28' 42" W), buoy #2 (42° 38' 45" N, 79° 56' 15" W), buoy #3 (41° 44' 25" N, 82° 27' 04" W)--see Figure 2; meteorological data from ship outings of the C.S.S. Limnos.

NWS surface meteorological data were for Erie, PA, Flint, MI, and Cleveland, OH; airport surface meteorological data for Burke Lakefront Tower, Cleveland, OH, Pittsburgh International Airport, Buffalo International Airport, and Toledo Express Airport; Coast Guard Marine Weather Log for Ashtabula Light Station, OH covering the dates of the Lake Erie cruises, July 22-28, Sept. 4-8, and October 16-20, 1979. We also obtained upper air soundings from the NWS stations at Buffalo, NY, Dayton, OH, Flint, MI, and Pittsburgh, PA.



LONDON
FLINT
SIMCOE
BUFFALO
CCIW #2
Long Point
Pointe-aux-Pins
CCIW #1
+R/V
CARSON
CCIW #3
ASHTABULA
TOLEDO
CLEVELAND
PITTSBURGH
0
50
75
100
Kilometers
43°
-42°
41°
40°
84°
83°
82°
81°
80°
79°

Figure 2. Location of R/V Rachel·Carson 55 km NNE of Cleveland (42°00'N, 81°30'W), and CCIW buoys #1, #2,

Micrometeorological data and aerosol samples were collected from aboard the USEPA's R/V Rachel Carson, anchored on station at 42° 00' N, 81° 30' W (Figure 2). This station is 55 km NNE of Cleveland, OH in the central basin of the lake, 2 to 5 km south of primary shipping lanes, and 42 km SE of Pointe aux Pins, Ontario. Thus, the sampling site was removed from major aerosol sources on shore, and upwind of the local (ship traffic) sources for a large percentage of on-station sampling time. The midlake sampling site has the advantages of: micrometeorological conditions that are representative of a large part of the lake's surface, long over water upwind fetches that enhance the likelihood that steady-state surface layer conditions prevail, and well-mixed aerosol populations in which no single anthropogenic source or pollution event is likely to dominate. If the lake surface appears constant to the air passing over it, the mass flux, F, within a well-developed surface layer is very likely to be constant throughout the vertical extent of that surface layer (Kraft, 1977).

To ensure that aerosol samples and meteorological data were not contaminated by the presence of the ship itself, all sampling was done in a bow-anchored mode. In that configuration, the ship faced bow-first into the wind, ± 15°. An open-beam lightweight aluminum boom extended 6 m ahead of the bow, at approx. 5 m above the mean water level (Figure 3). Meteorological sensors were placed at the forward end of the boom. Studies of bluff-body turbulence effects by Hunt and Mulhearn (1973) indicate that the 6 m boom was sufficiently long to avoid turbulence effects due to the ship structure. Turbulence intensity, $I_t = \sigma_u/\bar{u}$, where $\bar{u}$ is the running mean of wind speed and σ_u is the standard deviation about the mean, measured at the forward tip of the boom, ranged from 0.05 to 0.18, with a mean value of 0.11. This is comparable to the 0.02 to 0.14 observed by SethuRaman and Tichler (1977) from an air-sea interaction tower. Thus, very little increased turbulence was observed at the boom tip.

Two hi-volume air samplers were located on the boom, aft of the meteorological sensors. The hi-vols were 3 and 4 m ahead of the ship's bow. The filter holders and heads were silicone-rubber sealed to the

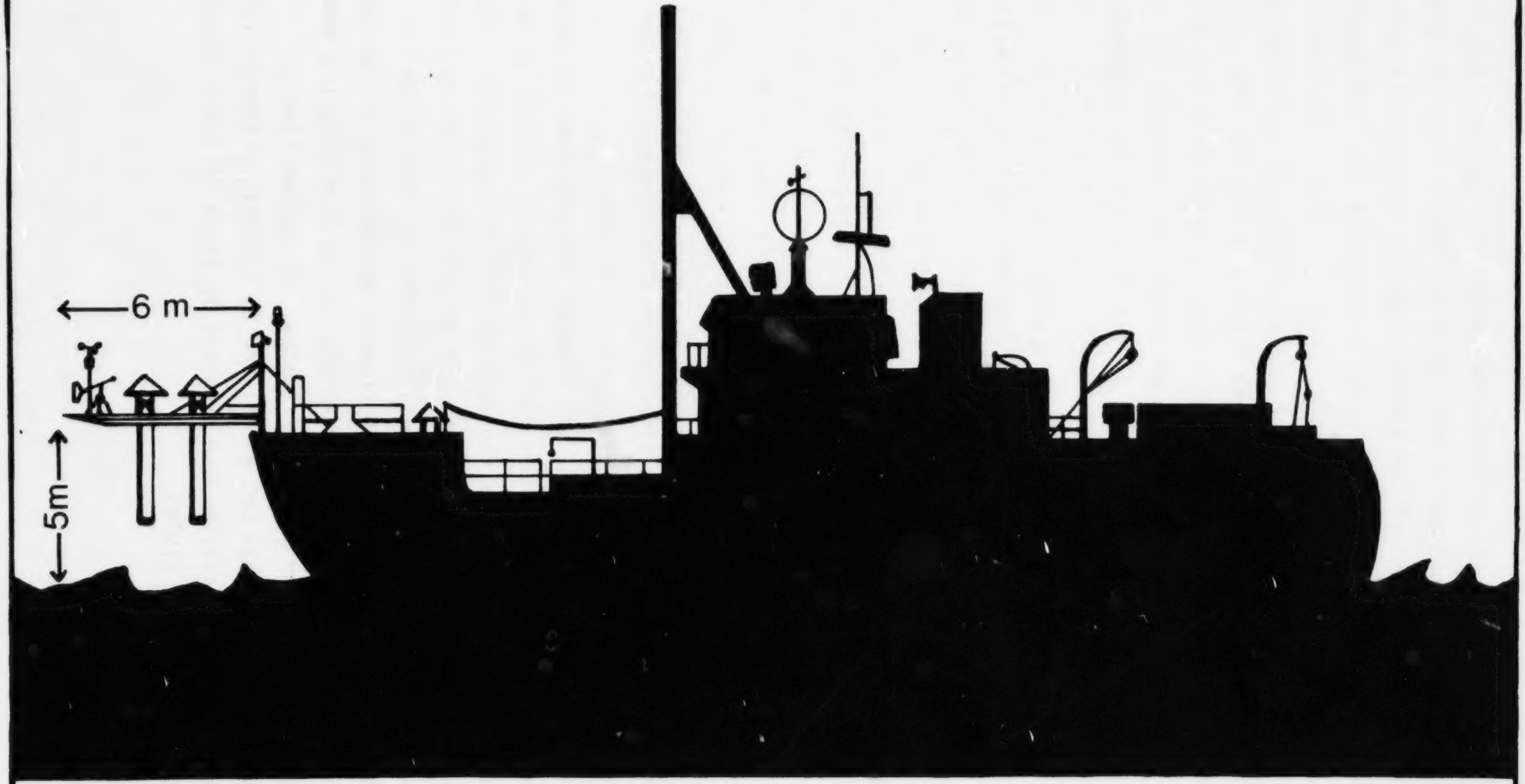


FIGURE 3: R/V Simons and Sampling Boom

pump motors. The pump exhausts were vented through 4-m long, 11-cm diameter plastic hoses which hung below the boom. This was done to prevent re-entrainment of the exhaust and contamination of aerosol samples. All hi-volume sampling was conducted either bow-anchored on station or, occasionally, while underway upwind. The possibility of contamination by the ship's diesel generator and engine exhausts was minimized. Whenever local wind direction (WD) shifted quickly to the point where the ship did not remain bow-first to the wind, hi-vol sampling was avoided. Continuous WD traces from the boom tip vane indicate that the boom remained ± 15° of directly upwind during all sampling periods.

Shipboard sampling was performed around the clock. In order to divide the data into manageable time segments, aerosol collection was kept to within 4-to 8-h segments. Each data set, because of this limited duration, correpsonds to a period of constant and readily characterizable meteorological conditions. The occurrence of rain intermittently precluded sampling during one cruise. At the beginning of each data set, all aerosol filters and impactors were replaced and bulk water samples were collected. Thus, the samples for chemical analyses can be classified according to values of meteorological parameters that prevailed during each data set. These results are then further classified in the context of climatologically expected frequencies-of-occurrence for those meteorological conditions.

In general, a minimum of 4-h elapsed time was used per data set in order to collect enough material on the hi-vol filters to be above the detection limits of the chemical analytical procedures. Past that minimum, rapid and persistent changes in the 5-m height monitored wind speed (u_5), WD, or thermal stability conditions were cause for the termination of a data set. Such changes were defined as two successive 15-minute mean values for any parameter being more than 1 σ removed from the running mean of that parameter. A maximum time of $\sim$ 8 h was allowed so that no data set was biased by a widely differing run time. Aerosol sample preparation and chemical analyses followed the procedures of Sievering et al. (1979).

Three optical aerosol sensors were located at the aft-most end of the boom. An Active Scattering Aerosol Spectrometer (ASAS) monitored aerosol number concentration in 60 size channels between 0.1 μm and 3.5 μm diameter. An Integrating Nephelometer (IN) gave a continuous output of aerosol backscattering coefficient, b_{scat}, which may be transformed into a measure of aerosol mass (M) concentration using the formula $b_{scat} = 0.3 + 0.014\ M$ (Davé et al., 1979). Finally, a condensation nuclei counter (CNC) provided relatively fast-response, large increase nuclei count indications of local aerosol sources (e.g., passing ships), in addition to monitoring ambient nuclei number concentrations.

In addition to the boom-mounted instruments, the forward part of the foredeck was the site of aerosol sampling. Two hi-volume samplers with type A glass fiber filters were run on overlapping schedules to collect aerosol mass concentration data. A third hi-vol on the foredeck was used with membrane filters to collect particles for optical analysis.

Surface layer thermal stability conditions were monitored by detailed measurement of vertical temperature gradients through the use of an array of matched and carefully intercalibrated fan-aspirated composite thermistor probes. These probes were mounted on a light mast at the bow, 10, 7, and 5 m above mean water level. The sensors were referenced to duplicate probes at the 5-m level. Statistically significant temperature gradients were observed during some data sets. Additional points in the vertical temperature gradient were measured by a hand-held infrared thermometer (IR) and a bucket thermometer. The IR was used to scan an area of the lake surface below the boom and, thereby, measure a surface temperature, T_0. The bucket thermometer measured lake water temperature at ∿1cm depth, T_W. The set and drift of surface water currents were calculated by observing the movements of drifters with an optical rangefinder, stopwatch, and hand-bearing compass. Air movements above the near surface layer at the ship were crudely observed during daylight hours by tracking 39-g pibal (PTE) balloons with a prism-viewing hand-held compass.

The pass-through experiment (PTE) was conducted during April to August, 1980 at Governors State University and at the City of Chicago 68th Street water intake crib on Lake Michigan. The PTE was designed to estimate, operationally, the overall particle collection efficiency of the modified Sierra 1, 3, 6 impactor using cellulose substrates/filter, the impactor/filter combination used during all Lake Erie and Lake Michigan sampling. Meteorological parameters were monitored during sampling, and continuous detailed records of temperature, relative humidity, and b_{scat} were kept.

Collection efficiency of the cellulose filter material for Pb, Fe, and Zn relative to the standard type A glass fiber filter was determined by running different multiple-filter assemblies on two hi-vols. On the first hi-vol, a type A glass fiber filter was placed 1 cm above a low-trace-element content (spectrograde, SG) glass fiber filter. The type A was used to gravimetrically find total aerosol mass concentration. The SG filter was hot acid leached (EPA procedure) and analyzed for Pb, Fe, and Zn by AA. On the second hi-vol of the simultaneously sampling pair, a modified Sierra 1, 3, 6 stage cascade impactor was used with cellulose impaction substrates filter. An SG filter was placed in line 1 cm behind the impactor. All four stages were prepared for Pb, Fe, Zn analysis.

The collection efficiencies determined here are relative to the type A because it is assumed that type A glass fiber is 100 percent efficient, i.e., lets no particles pass through. If this is true, or nearly so, then the SG backup of a type A should show concentrations near filter-blank level. The SG backup behind the less than 100 percent efficient cellulose filter should show concentrations at some level inversely related to the collection efficiency of the cellulose filter. Such multi-filter simultaneously collected pairs of filter sets were run on co-calibrated hi-vols. Filter exposure was at a flow-controlled rate of 1.13 m^3 min^{-1} (40 SCFM) for periods ranging up to 72 h. This length of time was required to allow sufficient material to pass through to the final SG backup for the chemical analysis.

3.2 EXECUTION OF THE SAMPLING PROGRAM

During the summer season, 1979 three cruises were conducted on Lake Erie. The USEPA R/V Rachel Carson anchored on station at 81° 31' W, 42° 00' N for several days during each cruise. A summary of shipboard sampling activities and description of meteorological conditions encountered follows:

The first cruise began 23 July 1979, with R/V Carson on site at 2300 CDT. The evening of 23 July 79, a weak surface front was situated north of Lake Erie. This was displaced to the northeast with the movement of an associated low pressure area. The morning of 24 July 79 was 80 percent overcast. There was some clearing at mid-morning, and by 7 PM CDT sky cover was only 50 percent. Several episodes of light rain interrupted sampling the evening of 24 July 79 through the next morning. By daybreak on 25 July 79, there was 90 percent cloud cover. Again, several episodes of rain occurred during the late afternoon and evening of 25 July. An associated low pressure system moved from northern Lake Michigan on the morning of 25 July 79 to the Quebec area by 26 July 79. This system trailed a cold front which passed through Lake Erie sometime earlier on the 26th. Ahead of the cold front passage, there was an increase of wind speed and the sky was entirely overcast the morning of 26 July 79. The sky began clearing 0900 CDT on 26 July 79. The night was very clear 27 July 79 and no further sampling was conducted.

Of the 78 hours on-site, about 72 hours were devoted to actual sampling. Four to 5 hours of the inactive time was due to periods of rainfall, during which all sampling temporarily halted; the remaining time was used in adjusting equipment and changing Hi-vol filters. Results from the aerosol data analysis indicate that the cruise covered two distinct aerosol regimes. Early in the cruise, the site was generally downwind of the Cleveland area and moderate aerosol mass concentrations (around 40 $\mu g\ m^{-3}$) were encountered. After passage of a cold front later in the cruise, the shift in winds brought about much lower aerosol concentrations, by two-fold. A total of twelve data sets were collected, each consisting of size-fractionated aerosol samples for metal and nutrient analysis, a bulk water sample, as well as physical aerosol and meteorological data.

This cruise period was one of generally steady, moderate winds in the range of 3 to 6 $m\ s^{-1}$. Atmospheric temperature stability throughout the period may be characterized as neutral to slightly stable, $\Delta T = (T_{air} - T_o) = 0.1$ to 1.5°C.

The second cruise began 5 Sept 79. This cruise was shortened first by late arrival of the ship at Cleveland and later by heavy weather encountered 7 Sept 79. The weather during the entire second outing was influenced by the presence of hurricane David. On the morning of 5 Sept 79, Lake Erie was under the influence of a broad Great Lakes high pressure area. By the time sampling was started, winds at the sampling site were from the ENE at about 5 $m\ s^{-1}$. High cirrus provided a 90% cloud cover and the horizon was very hazy. Winds dropped to about 3 m s^{-1} during the night and shifted to the north--but as David progressed up the East Coast, the speed increased steadily reaching 7 m s^{-1}. The wind direction became progressively more westerly, being almost due west at 1200 CDT on 6 Sept 79 and WSW by the early afternoon. Some light rain was encountered during the late afternoon of 6 Sept 79.

The windspeed began to drop again during the evening and the wind direction moved to NNW. Winds were too light to do any sampling from about 0000 CDT to 0100 CDT on 7 Sept 79 when the wind picked up from the NNW. Near sunrise the sky cover was about 30 percent. This cover increased through the remainder of the day, becoming about 80 percent in the afternoon. Visibility was, however, exceptionally good. Near 1200 CDT on 7 Sept 79, the wind shifted to the WNW and began to increase. By 1500 CDT, winds were over 10 m s^{-1}.

Of the 49 hours on-site, 45 hours were devoted to actual sampling; there was a total of 3 hours of rain delays and low wind speeds when no sampling could be done. Less than one hour was necessary for on-site equipment adjustments and filter changes. A total of eleven data sets were collected on this cruise. This period was one of prevailing winds from the northern shore of Lake Erie, and aerosol mass concentrations of 10-25 $\mu g\ m^{-3}$ were indicated by the Integrating Nephelometer.

This cruise ended short of the time scheduled. At about 1400 CDT on 7 Sept 79 the wind speed sharply increased from a 5-6 m s^{-1} range to a 10-13 m s^{-1} range; wave heights promptly increased from less than 1 m to 3-5 m. For reasons of personnel safety and prevention of permanent damage to equipment the ship weighed anchor and departed station at about 1700 CDT on 7 Sept 79.

The third and last cruise on Lake Erie began 16 Oct 79, with the Carson arriving on site at about midnight. At the beginning of the cruise, Lake Erie was Southeast of a rapidly occluding front. This brought small amounts of scattered rain and a generally overcast sky. Winds were 5-6 m s^{-1} from the SW. As the system passed over the lake, winds dropped to 2 m s^{-1} with a wind shift to the NW accompanied by some clearing. By 2100 CDT on 16 Oct 79, winds had shifted to ENE and were increasing. 17 Oct 79 was overcast except for a brief period of partial clearing in the morning. That evening, the lakes began to feel the influence of a well-developed low pressure system west of the lakes. The leading warm front swept over Lake Erie that night. The pressure dropped rapidly and winds increased dramatically to 8-10 m s^{-1}. The morning of 18 October 79, the sky was clear, but overcast again by 1100 CDT.

All of the 65 hours on-site were spent in sampling. No rain delays were necessary despite scattered showers in the area; overlapping aerosol data sets contributed to the 100% efficiency of on-site sampling time. A total of thirteen data sets were collected. Aerosol concentration during this cruise period was moderate, in the 30-80 μg m^{-3} range. Wind speed and direction were, as previously described, quite variable. Atmospheric temperature stability was neutral to unstable, $\Delta T = 0$ to 0.2°C.

SECTION 4
DATA, ANALYSIS AND BASIC RESULTS

4.1 AEROSOL ELEMENTAL DATA

One immediately obvious factor in examining the aerosol trace element data is that concentrations over Lake Erie were relatively low, compared to expectations based on Lake Michigan data. Despite longer average filter run times during the Lake Erie cruises, almost all samples initially fell below the inductively coupled argon plasma atomic emission spectroscopy (ICAP) detection limits set by USEPA-CRL. Upon careful examination of the raw (no detection limit) ICAP data a SEPA rate series of reagent blanks, filter blanks, field blanks, and spike samples were calculated. This led to the determination of detection limits ($\bar{c} + 3\cdot\sigma$ of lab DI water samples) for this group of samples far below the USEPA-CRL values. That calculation resulted in the recovery of many data points which had been thought to be lost in the ICAP instrumental noise. The filter field blank corrections ($\bar{c} + \sigma$) were also determined and analyses of replicates indicate a mean reproducibility of about 20 percent or better for ten elements, even at these low levels (Table 1). Typical sample values, also in Table 1, were derived from overall averaged concentrations and run times. Because the typical sample concentrations are not always too far above the filter blanks, it is difficult to justify, with statistical significance, the examination of the ICAP data in individual data set by data set cases. It is more reasonable to aggregate several data sets, based on similar values of defining parameters, and discuss mean concentration values for the group of sets. Recovery studies show that >90% for all except Al, for which 50-70% recoveries were determined. Al concentrations determined by ICAP were enhanced by a factor of 60% to compensate for its poor recovery.

Table 2 is based on all data sets collected at mid-Lake Erie during the summer and fall of 1979. The overall geometric mean concentrations are given for those elements which appeared above detection limits and blank corrections in 75 percent or more of the data sets. These mean concentrations are generally a factor of three to eight lower than the concentrations observed over Lake Michigan during 1977.

Table 1. ICAP BLANKS, DETECTION LIMITS, AND TYPICAL SAMPLE ($\mu g\ l^{-1}$)

	Field Blank ($\bar{c} + 1 \cdot \sigma$)	Detection Limit ($\bar{c} + 3 \cdot \sigma$)	Typical Sample
Al	85	0.8	180
Ba	12	0.1	20
Cd	2.8	0.3	22
Cu	44	2.5	105
Cr	6.6	0.1	18
Fe	180	2.0	380
Mn	4.7	3.4	15
Ni	0.3	3.3	42
Pb	11	7.6	32
Ti	2.9	0.3	12
Zn	59	9.0	330

Table 2. MID-LAKE ERIE AEROSOL, GALE 1979 SETS

	$\bar{C}$,[†] ng-m^3	F/C[†]	M%	EF[**]	EF_{LM}[**]
Al	35[*]	1.9	0.1	=1.0	=1.0
Ba	1.2	4.8	.004	8.0	3.5
Cd	2.0	7.4	.006	2900	1800
Cu	10.4	4.3	.03	1100	120
Cr	1.8	3.4	.004	3.3	n.d.
Fe	46	2.0	0.13	2.4	2.1
Mn	0.8	2.2	.003	2.0	5.9
Ni	3.0	2.6	.01	140	230
Pb	3.5	6.2	.01	720	3200
Ti	1.0	1.2	.003	0.8	0.9
Zn	37	6.3	0.11	1500	320

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[*] Includes 60% enhancement due to poor analytical recovery.

[†] Corrected for pass-through filter loss.

[**] Approximate due to Al recovery problem.

It is important to interject here the results of the pass-through experiment (PTE). It was found that 37 ± 7% of Pb, 32 ± 6% of Zn and 12 ± 3% of Fe collected on the backup filter passes on through that filter. A significant correction factor must, then, be applied to the observed concentrations. This has been done in Table 2 by accounting not only for pass-through losses but also the 5% cascade impactor wall loss of small particles identified by the impactor manufacturer (Sierra). Other parameters describing the composite of the aerosol also seem quite interesting for Lake Erie. Values of the fine to coarse (F/C) aerosol ratio are calculated as

$$F/C = \frac{\bar{c}\ (\text{backup filter, } D < 1.0\ \mu\text{m})}{\bar{c}\ (\text{1st stage impactor, } D > 1.0\ \mu\text{m})}\ .$$

The elemental mass percent (M%),

$$M\% = \frac{\bar{c}\ (\text{trace element})}{\bar{c}\ (\text{total aerosol})}$$

values are much lower than the corresponding values for the Lake Michigan aerosol. However, enrichment factors, EF, based on Bowen's (1966) midwestern soils with Al as the indicator element, correspond fairly well with the Lake Michigan aerosol data (Table 2). This may suggest some similar source types for both sites, with added source modification or transport-dependent processes affecting the Lake Erie data.

In order to examine the differences in aerosol composition parameters more closely, back-trajectory plots were used to group data sets having similar source regions. Figures 4 and 5 are examples of the trajectory plots, showing horizontal extent and vertical depth of the most probable source regions for each set. Figure 6 is a summary of all plotted trajectories, showing the most likely 24-hr averaged plots. From these data, each of the sets was grouped into one of four general source regions. On the U.S. side of the lake, all non-Cleveland area trajectories were labelled US-rural. All sets from the Canadian side were called Canada-rural, while all trajectories that did not reach shore within 24-hr are "Lake" sets. Finally, those data sets obtained while the ship was directly downwind of Cleveland were grouped together. The approximate ship-to-shore compass sectors for each of these four source regions is: US-Rural, 60°-190°; Lake, 240°-260° and 20°-60°; Canada-Rural, 260°-20°; and Cleveland, 190°-240°. The mean concentration data (Table 3) for each

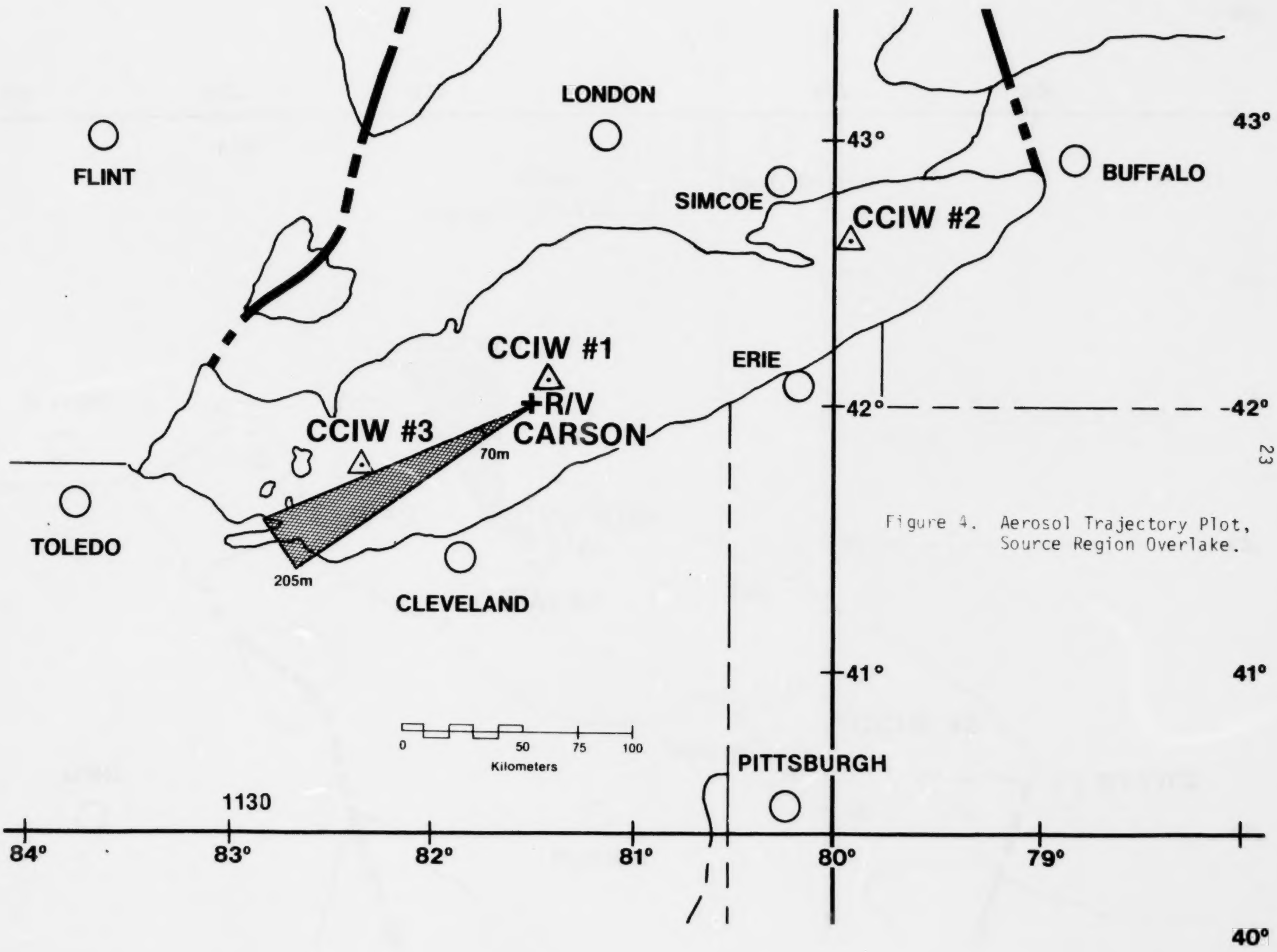
FLINT
LONDON
SIMCOE
BUFFALO
CCIW #2
CCIW #1
ERIE
+R/V
CARSON
CCIW #3
70m
TOLEDO
205m
CLEVELAND
0
50
75
100
Kilometers
PITTSBURGH
1130
43°
43°
42°
-42°
41°
41°
40°
84°
83°
82°
81°
80°
79°

Figure 4. Aerosol Trajectory Plot, Source Region Overlake.

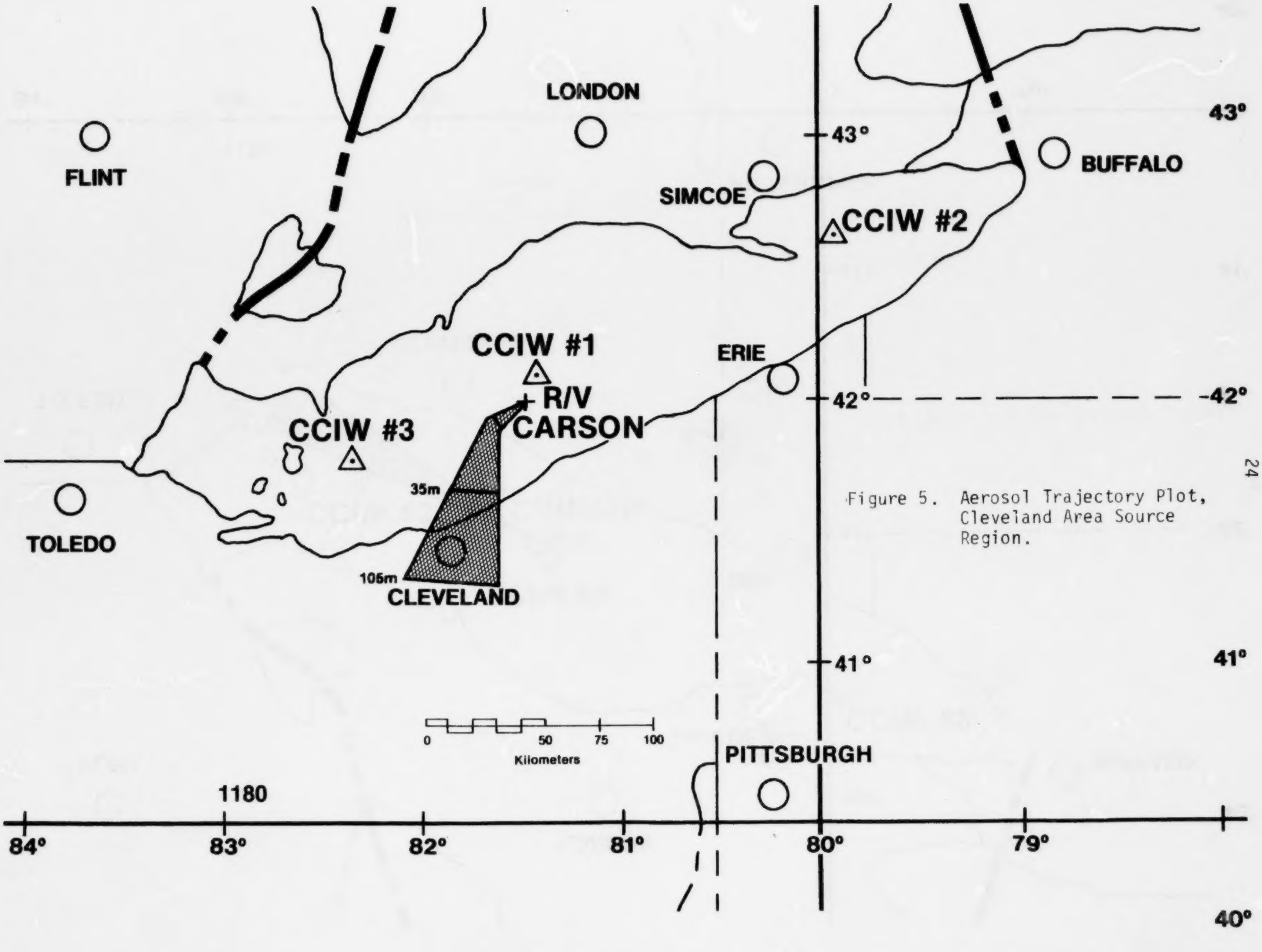
LONDON
FLINT
SIMCOE
BUFFALO
43°
43°
CCIW #2
CCIW #1
ERIE
R/V
CARSON
42°
-42°
CCIW #3
TOLEDO
35m
105m
CLEVELAND
41°
41°
0
50
75
100
Kilometers
PITTSBURGH
1180
84°
83°
82°
81°
80°
79°
40°

Figure 5. Aerosol Trajectory Plot, Cleveland Area Source Region.

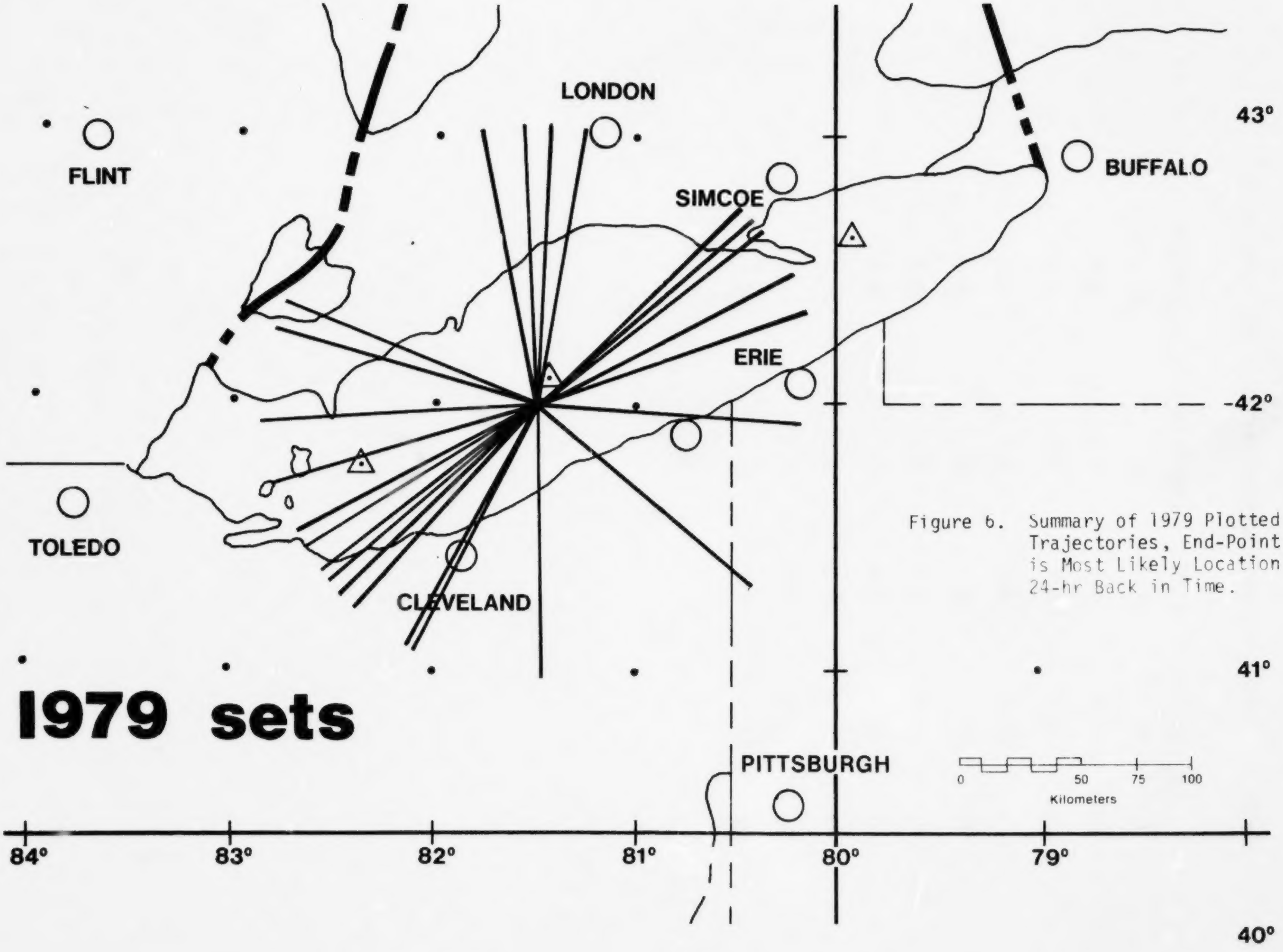
1979 sets
FLINT
LONDON
SIMCOE
BUFFALO
ERIE
TOLEDO
CLEVELAND
PITTSBURGH
43°
-42°
41°
40°
84°
83°
82°
81°
80°
79°
0
50
75
100
Kilometers

Figure 6. Summary of 1979 Plotted Trajectories, End-Point is Most Likely Location 24-hr Back in Time.

Table 3. GEOMETRIC MEAN CONCENTRATIONS, GALE 1979 SETS, ng m^{-3}

	US-Rural	Lake	Canada-Rural	Cleveland
Al	27	26	25	55
Ba	3.3	0.5	1.4	2.4
Cd	1.9	0.4	0.1	3.6
Cr	0.6	0.8	4.1	1.5
Fe	17	30	59	74
Mn	1.0	0.8	0.3	0.8
Ni	0.7	0.4	0	0.7
Pb	2.2	2.6	0.2	11.
Ti	0.3	0.3	0.3	1.0
Zn	18	36	13	147

of these source regions contains no surprises. That is to say, the Cleveland source clearly dominates, especially given the prevailing winds in this area. Note that the mean concentration of Pb and Zn in the Cleveland source is more than twice that from all three other source regions combined. Additional information about each source region is obtained from the ASAS data. Figures 7 and 8 are plots of aerosol volume distribution, from the ASAS data, which show distinct differences between the lake and Cleveland source regions. The lake region source has a clear bimodality suggesting that two separate source types contribute, the small aerosol ($\tilde{r}$ of 0.1-0.2 μm) source may be similar to the Cleveland aerosol source. The large aerosol ($\tilde{r}$ of 0.4-0.5 μm) source may be the lake itself. A discussion of the Great Lakes as an aerosol source is found in Appendix D.

4.2 DEPOSITION VELOCITY PARAMETERIZATION

The largest single uncertainty in Great Lakes atmospheric loading estimates--despite efforts to reduce it--remains the estimation of a deposition velocity, v_d. Progress over the last two years has been made on the modeling of the deposition process and some data on deposition velocity as a function of aerosol diameter, v_d (D) were obtained over Lake Michigan. Yet, the uncertainty in v_d (D) is still nearly an order of magnitude for $0.02 < D < 2$ μm. Indeed, the summary table in the Executive Summary of the Lake Michigan final report (EPA 905/4 - 79 - 016) would be better to have the columns "minimum dry deposition" and "mean dry deposition" retitled to read "moderate estimate" and "high estimate," respectively. This less accurate statement of loadings is the result of a more sophisticated understanding of the deposition process obtained by our parameterization efforts as well as the modeling efforts by the Slinns and by Hicks and Williams. Slinn and Slinn (1980) have assessed the contribution of particle growth in high RH environments and Hicks and Williams (1980) have added the effects of diffusion, sedimentation and growth to their own analysis of whitecapping and subsequent lake capture of airborne particles by reducing surface transfer resistance to zero over that percentage of the surface where whitecapping exists. Both of these modeling efforts suggest a fairly strong dependence of v_d on

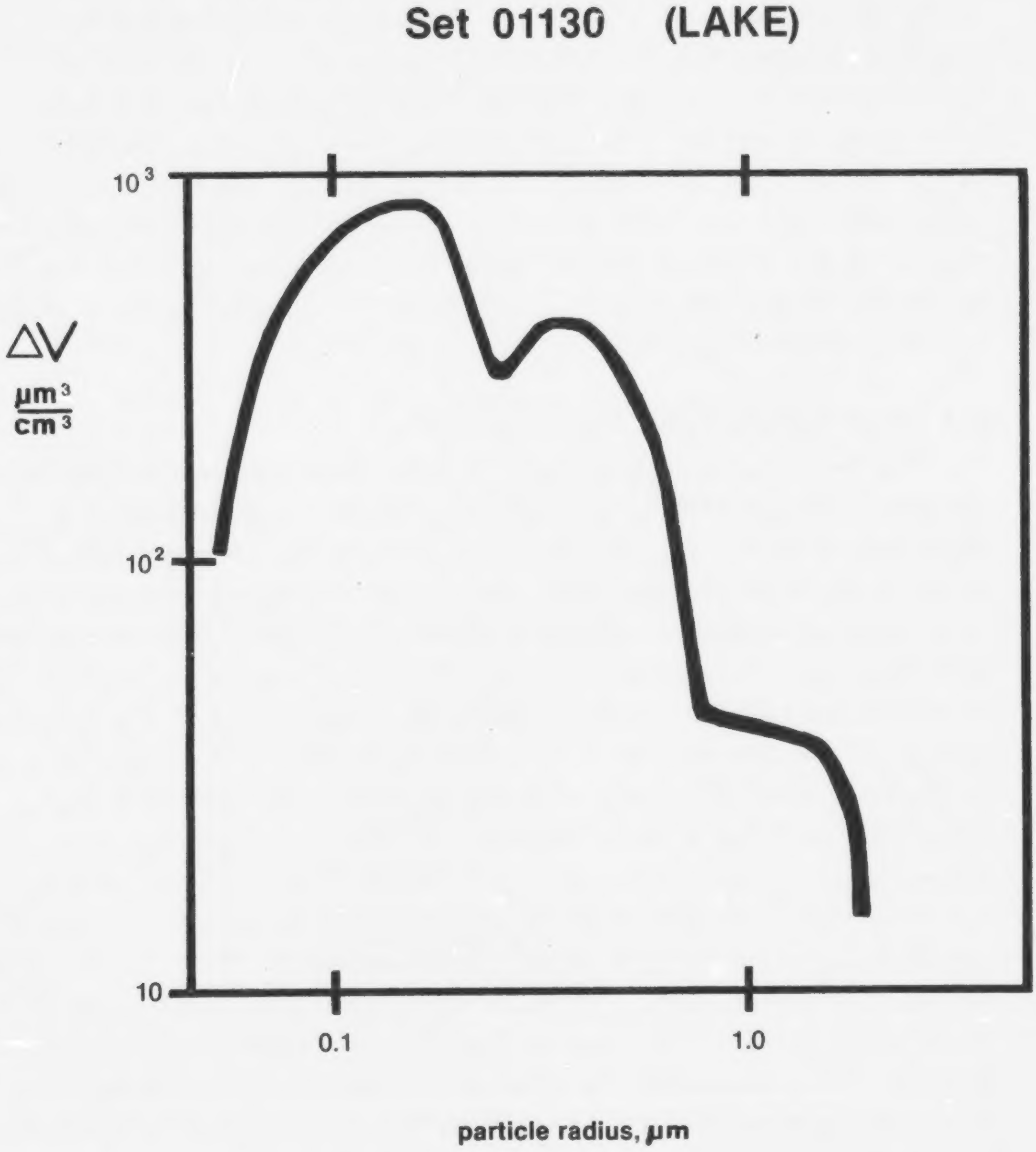

Figure 7. Aerosol Volume Distribution Plot for Overlake Trajectory Case.

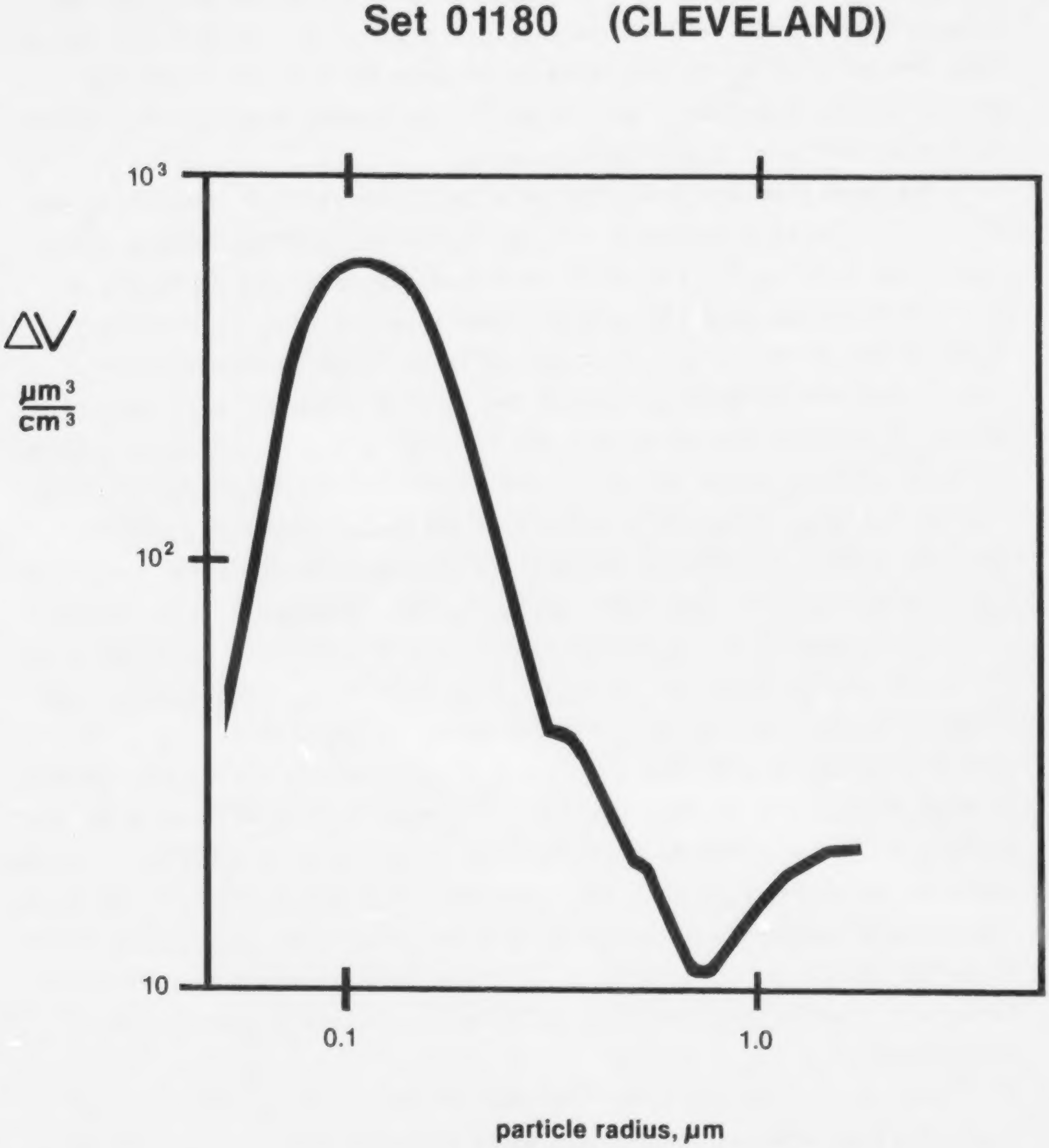

Figure 8. Aerosol Volume Distribution Plot for Cleveland Source Region Trajectory Case.

D in the $0.1 < D < 1$ μm particle size range, as have previous modeling efforts. Our parameterization has accounted for what meager data is available on v_d (D). Limited profile sampling while aboard the R/V Simons on Lake Michigan in 1977 showed that v_d varied by only two- to threefold in the $0.1 < D < 1$ μm particle size range. It was also found that the ratio of v_d to the aerodynamic transfer velocity (transfer controlled by turbulence) was 1/3 to 1/2 for eleven moderate wind speed ($2.4 < \bar{u} < 8.2$ m s^{-1}) profile data sets.

Any mechanism which results in a small variation in aerosol v_d for $0.1 < D < 2$ μm is a candidate for explaining the profile results above. Conditions near to the air/water interface are portrayed in Figure 9. Here, the surface layer is seen as three separate zones: a turbulent layer, a buffer layer and a viscous sublayer. The turbulent layer constitutes the largest portion of the surface layer depth of several meters to several tens of meters and here $v_d^{-1} = r_a$. A continuous viscous sublayer enveloping all or nearly all of the surface roughness elements follows the gross observable contour of the water's surface. Mass transfer within the viscous sublayer is dominated by molecular transport, i.e., Brownian motion (for small particles less affected by gravitation). The buffer layer is a transition zone in which turbulence is reduced by the close proximity of the surface. Both turbulence-induced eddies and Brownian motion contribute to mass transfer in the buffer layer. As higher wind speeds and less stable air prevail within the surface layer, a rough flow regime becomes dominate [Figure 9 (b)] in which many of the surface roughness elements protrude outside of a now discontinuous viscous sublayer resulting in a more efficient path for mass transfer. The wind speed and/or temperature stability at which this rough flow regime occurs is quite uncertain. Yet it is certain that under rough flow conditions turbulent transfer and impaction will increase overall mass transfer substantially.

Kondo et al. (1973) found that 30% of the roughness elements due to high-frequency components of ocean waves protrude outside the viscous sublayer at $\bar{u}_{10} = 2$ m s^{-1} wind speeds. At $\bar{u}_{10} = 8$ m s^{-1} Kondo et al. (1973) found that over 99% of the high-frequency roughness elements protrude outside the remaining discontinuous sublayer. These percentages should not be very

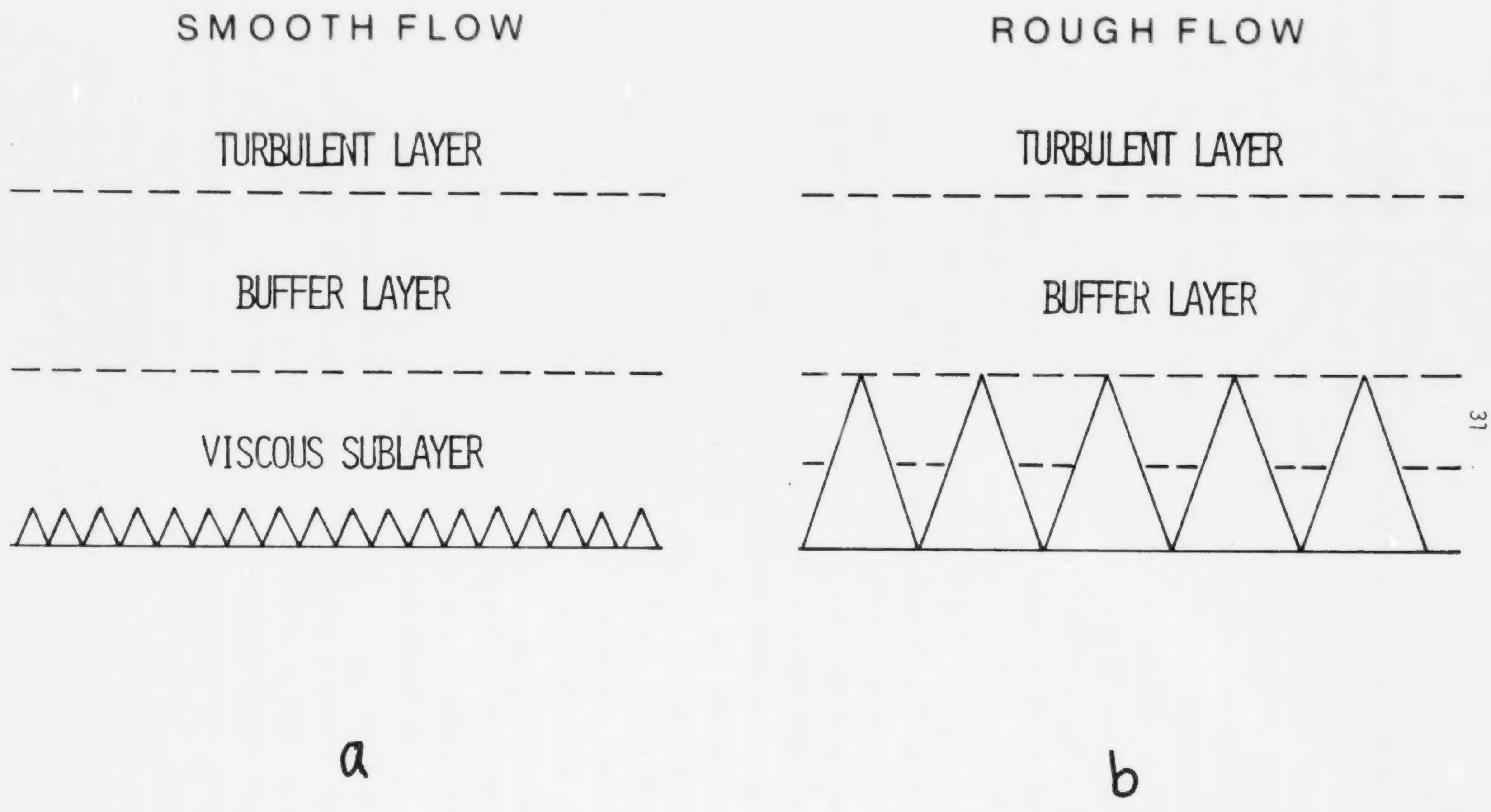
SMOOTH FLOW
TURBULENT LAYER
BUFFER LAYER
VISCOUS SUBLAYER
a
ROUGH FLOW
TURBULENT LAYER
BUFFER LAYER
b

Figure 9. Diagrammatic Representation of the Surface Layer Above the Air-Water Interface: (a) Smooth flow; (b) Rough flow.

different for the surface of Lake Michigan. From a physical viewpoint it must be concluded that the ratio of the height of the protrusions, h_s, to the viscous sublayer thickness should be an important factor for smooth or rough flow dominance (Schlichting, 1968). Since 30% of the high-frequency wave components can be expected to protrude outside the sublayer at 2 m s^{-1} and the mean surface roughness height may equal the viscous sublayer thickness at 3 m s^{-1}(Kondo et al., 1973), smooth flow conditions may not prevail above 2 m s^{-1} and probably not above 3 m s^{-1}. Kondo et al. (1973) found the roughness Reynolds number range for transition from smooth to rough flow as $6 < u_* h_s / \nu < 67$, where u_* is the friction velocity and ν the kinematic viscosity. SethuRaman (1979) found $20 < u_* h_s / \nu < 75$ for this transition region at a stabilized buoy off Long Island. This descrepancy with Kondo et al. (1973) suggests the transition region may not be encountered until $\bar{u}_{10}$ reaches 4 or 5 m s^{-1}. However, SethuRaman (1979) restricted his analysis to cases when the waves propagated in the same direction as the wind. In the $2 < \bar{u}_{10} < 5$ m s^{-1} range, wind speed and especially wind direction variability increase. As a result, the "aged-wave" condition which SethuRaman (1979) considered may not prevail. Indeed, Donelan (1977) found drag coefficients (C_D) of 15 x 10^{-3} and larger in the developing wave condition and "a pronounced minimum in this drag coefficient as the wave field approached maturity." Boutin et al. (1977) found a direct dependence of the drag coefficient upon wind speed variability below $\bar{u}_2 = 4$ m s^{-1} with resultant drag coefficient mean and standard deviation of 1.8 and 1.3 x 10^{-3}, respectively. Wind speeds were in the $1.2 < \bar{u}_2 < 3.6$ m s^{-1} range.

Fully rough flow for aerodynamic transfer is usually assumed to prevail at $\bar{u}_{10} = 8$ m s^{-1} and above, whereas one may expect a transition flow between 3 and 8 m s^{-1}, and smooth flow below 3 m s^{-1}. It has been stated that aerodynamic transfer can be expected to be larger (possibly much larger) than mass transfer in the buffer layer during transition and smooth flow because of what is known as the bluff body effect (Chamberlain, 1966). In the immediate vicinity of the surface, transfer to the surface is controlled by skin friction and pressure forces, caused by fluid impacting on the roughness elements of the surface. Transfer by pressure forces at the surface is known as form drag and since there is no apparent analogue in mass transfer, a possibly severe limitation of the near equality between aerodynamic and mass transfer is encountered within the buffer layer and especially the viscous syblayer.

However, Wu (1979) has shown that the "young-wave" condition observed by Donelan (1977) and Boutin et al. (1977) can generate gravity-capillary waves at wind speeds of 2-3 m s^{-1}. This could explain the occurrence of high frequency wave protrusion through the viscous sublayer at $2 < \bar{u}_{10} < 3$ m s^{-1}. Further, Owen and Thomson (1963) have shown that horseshoe eddies wrap themselves around the individual roughness elements for those that are closely spaced. Such eddies can be expected to result from high-frequency wave components. If we now reconsider the data of Kondo et al. (1973), it does not seem unlikely that transfer through the buffer layer and impaction to the roughness elements within a discontinuous viscous layer induce a low-resistance path for particle transfer when compared to molecular diffusion transfer within the viscous sublayer. This path may be available to only a few of the particles in the buffer layer but may nonetheless be a relatively efficient transfer path even at 2 m s^{-1} wind speeds. Further discussion may be found in Sievering (1981).

The above discussion indicates that $u_* h_s/\nu$ may be a key parameter in the estimation of aerosol v_d over the Great Lakes, h_s, the characteristic height of water surface roughness elements is the only unknown in this parameter. By following the reasoning of Kitaigorodskii (1973) h_s can be stated as

$$h_s = \left(\frac{3}{4} \pm \frac{1}{4}\right) \frac{u_*^2}{g}$$

where g is the gravitational constant, 9.8 m s^{-2} and u_*, again, is the friction velocity. u_* may itself be approximated as $\frac{\bar{u}}{30}$ so that we can approximate h_s over Great Lakes surfaces as a function which is proportional to the third power of the mean wind speed during any one filter sampling set. During rough flow conditions we may still assume v_d to equal aerodynamic transfer ($v_d = \bar{u} \cdot C_{DD}$, where C_{DD} is the stability corrected drag coefficient--see App. B of the Lake Michigan final report). Further, from the Lake Michigan profile results we can estimate v_d to be 1/3 to 1/2 of $\bar{u} \cdot C_{DD}$ during moderate flow conditions. We will continue to assume $v_d = 0$ under smooth flow conditions. Table 4 shows, then, the parameterization resulting from our consideration of the available (meager) experimental data plus theoretical arguments.

Table 4. PARAMETERIZATION OF DEPOSITION VELOCITY, v_d

$\frac{u_* h_s}{\nu}$	v_d	# of Lake Erie Sets
0-10	0	5
10-25	(1/8 to 1/4) . $\bar{u}$. C_{DD}	8
25-50	(1/3 to 1/2) . $\bar{u}$. C_{DD}	7
50-70	(2/3 to 3/4) . $\bar{u}$. C_{DD}	6
>70	1 . $\bar{u}$. C_{DD}	2

The available data on $\frac{u_* h_s}{\nu}$ versus flow condition indicates that the range of values between 10 and 25 to be indefinite as to smooth or moderate and 50-70 indefinite as to moderate or rough. Thus, the parameterization in Table 4.

Of the twenty-eight filter sets obtained at mid-Lake Erie (not counting the three sets obtained while steaming back to dock), the number falling into each of the $\frac{u_* h_s}{\nu}$ ranges is shown in the last column of the table. The overall Lake Erie average $v_d \approx 0.35$ cm s^{-1} obtained by this parameterization may be seen to be less than half the 0.75 cm s^{-1} had $v_d = \bar{u} \cdot C_{DD}$ been used.

To this point in the parameterization we have not dealt with the particle size dependence of v_d. Partly this is because the Lake Michigan profile results (Sievering, 1981) suggest a small ($\sim$ twofold) correction. Alternatively, a review of Slinn and Slinn (1980), Hicks and Williams (1980), and, more recently, Williams (1981) on the contribution of particle growth in 100% RH environments--as over the Great Lakes--suggests that for particles of $D > 1$ μm, v_d equals the aerodynamic transfer velocity ($\bar{u} \cdot C_{DD}$). Since our Great Lakes aerosol sampling obtained elemental mass concentration in the $D > 1$ and $D < 1$ μm size fractions the parameterization of Table 4 is to be applied only to the $D < 1$ μm aerosol fraction. For $D > 1$ μm it is assumed, as part of this overall parameterization, that $v_d = \bar{u} \cdot C_{DD}$.

SECTION 5

INTERPRETATION OF RESULTS

Our approach to interpretation throughout this three-year Lake Erie research effort has focused on the preparation of articles for scientific peer review with hoped for publication in refereed journals. Two articles already published are: 1) Profile Measurements of Particle Mass Transfer at the Air-Water Interface, Atmospheric Environment, vol. 15, No. 2, pp. 123-129 (1981); 2) Air-Sea Particle Exchange at a Nearshore Oceanic Site, Journal of Geophysical Research, vol. 87, No. C13, pp. 11027-37 (1982). Several articles are either under review or still in preparation. For this reason they are appendices to this research report. In order of appearance in the appendices they are (with note in parens on status and journal): A) Lake Breeze Effects on Particle Size Spectra and Sulfate Concentration over Lake Michigan (submitted reviewed and being revised for publication in Journal of Applied Meteorology); B) Chemical Uniformity of Atmospheric Aerosol: Its Violation at a Mid-Lake Erie Site (submitted to Atmospheric Environment); C) Tech. Note: Trace Element Pass-Through for Cellulose Impactor Substrates and Filters When Used for Aerosol Collection (not yet submitted for review); D) Chemical Elements in Atmospheric Aerosol over Southern Lake Michigan: The Contribution of the Lake Source (submitted, reviewed and being revised for publication in Journal of Great Lakes Research); and E) Some Effects of Wind-Shift on Over-Lake Turbulence and Aerosol Deposition. All these appendices will be referenced at various points in this Interpretative Section. A few points of major concern to this USEPA report will not be submitted for publication elsewhere and are, therefore, discussed in some detail below.

5.1 SHIP/BUOY METEOROLOGICAL DATA INTERCOMPARISON AND THE REPRESENTATIVENESS OF SHIP SAMPLING

Is ship sampling at one point and for relatively brief time periods representative of the whole lake's meteorology and climatology? The Lake Erie sampling program provided a unique opportunity to assess the question of ship versus whole lake meteorology thanks to the Canada

Center for Inland Waters (CCIW). CCIW has deployed three buoys on Lake Erie as shown in Figure 2. The intercomparison of buoy #1 with ship sampled meteorological data is of interest. Yet, of greater interest is the intercomparison of the three buoys' meteorological data during the three ship sampling periods, since this intercomparison affords us the opportunity to consider how meteorologically representative is the ship's location.

Buoy-gathered data were taken at the three Lake Erie sites previously mentioned. When looking at these data several points should be kept in mind. The measurement height was not specified but appears (from photos) to be from 1 to 2 m. The buoy data were taken such that hourly-averaged values are centered on the hour whereas ship data result in hourly averaged values centered 7.5 minuter before the hour. Only temperature, wind speed and direction are here considered since they are very likely the meteorological parameters most important in lake loading estimates.

Inspection of the data reveals several periods when the buoy intercomparison shows large discrepancies but fewer periods and smaller discrepancies between ship and buoy #1 located less than 10 km apart. Indeed the difference between ship and buoy #1 for wind speed and temperature averaged across one-hour periods only very rarely results in a more than 5% difference in the bulk Richardson number (proportional to wind speed squared divided by temperature). This difference in calculated Richardson number was never more than 8%. We may conclude differences between ship and buoy #1 data are primarily related to instrumentation measurement errors. The larger discrepancies between ship (or buoy #1) data at central Lake Erie and those data obtained by buoy #2 or #3 at the western and eastern ends of Lake Erie are more likely due to synoptic or mesoscale meteorological differences.

There were a few cases where the buoys reported similar values, but with a lag time between them indicating a westward or eastward moving disturbance. These were for temperature: 25 July 4:00 to 6:00; 5:00 to 10:00, 6 Sept and for wind speed: 25 July 4:00 to 12:00; 28 July 8:00 to 12:00; 6 Sept 12:00 to 17:00; and 17 Oct 6:00 to 13:00. Times are local. These disturbances are as would be expected with frontal passages and require no further comment. However, a few cases did not seem to be associated with synoptic disturbances. These generally had a large spread among the three buoys. For wind speed: 26 July 21:00 to 27 July 11:00; 6 Sept 14:00 to 7 Sept 15:00; 17 Oct almost all of the 24-hr period; 18 Oct 14:00 to 24:00; and for temperature: 26 July 7:00 to 27 July 4:00; 5 Sept 2:00 to 6 Sept 10:00; 17 Oct 4:00 to 16:00. The similarity of these periods of discrepancy with each other for both wind speed and temperature point to other than instrumental problems. They are most likely due to lake/mesoscale effects. Depending on whether one considers wind speed or temperature these periods represent 13-23% of the whole overall, though, the meteorological data taken at the ship are representtive of the entire open water area (i.e., removed from nearshore) of Lake Erie except, of course, when synoptic disturbances are present.

Regarding the question, is ship sampling representative of lake climatology, a chi-square test was applied to compare the ship station observations of wind speed, wind direction and thermal stability (i.e., air-water temperature difference) with the ten-year NOAA Lake Erie Climatology (Summary of Synoptic Meteorological Observations for Great Lakes Areas, Vol. 1, Lake Ontario and Lake Erie). Data on wind speed and thermal stability were grouped into five bins each (thus, 4 degrees of freedom) and for wind direction into eight bins (7 degrees of freedom). Chi-square values are 42,38 and 11 for wind speed, thermal stability and wind direction, respectively, indicating that we can accept, with only 0.1%, 0.2% and 25% probability, the hypothesis that there is no difference between ship-sampled and annualized climatological data on Lake Erie wind speed, thermal stability and wind direction, respectively. When only June, July, and October climatological data are considered the probabilities increase to 5%, 10% and 40%. These very low probabilities indicate that a very poor representation of Lake Erie climatology was observed during ship sampling during June, July, and October of 1979. This is especially so regarding the under-represented high wind speeds (> 9 m s^{-1}) which occur 12% of the climatologically average year and unstable thermal conditions which occur nearly 40% of the climatologically average June, July, and October as well as the climatologically average year. A cumulative frequency plot of the ship-sampled wind speed regime (ship sample) versus the lake's climatologically average wind speed regime is shown in Figure 10 (with Lake Michigan wind speed regime also shown). The Southwest (primarily

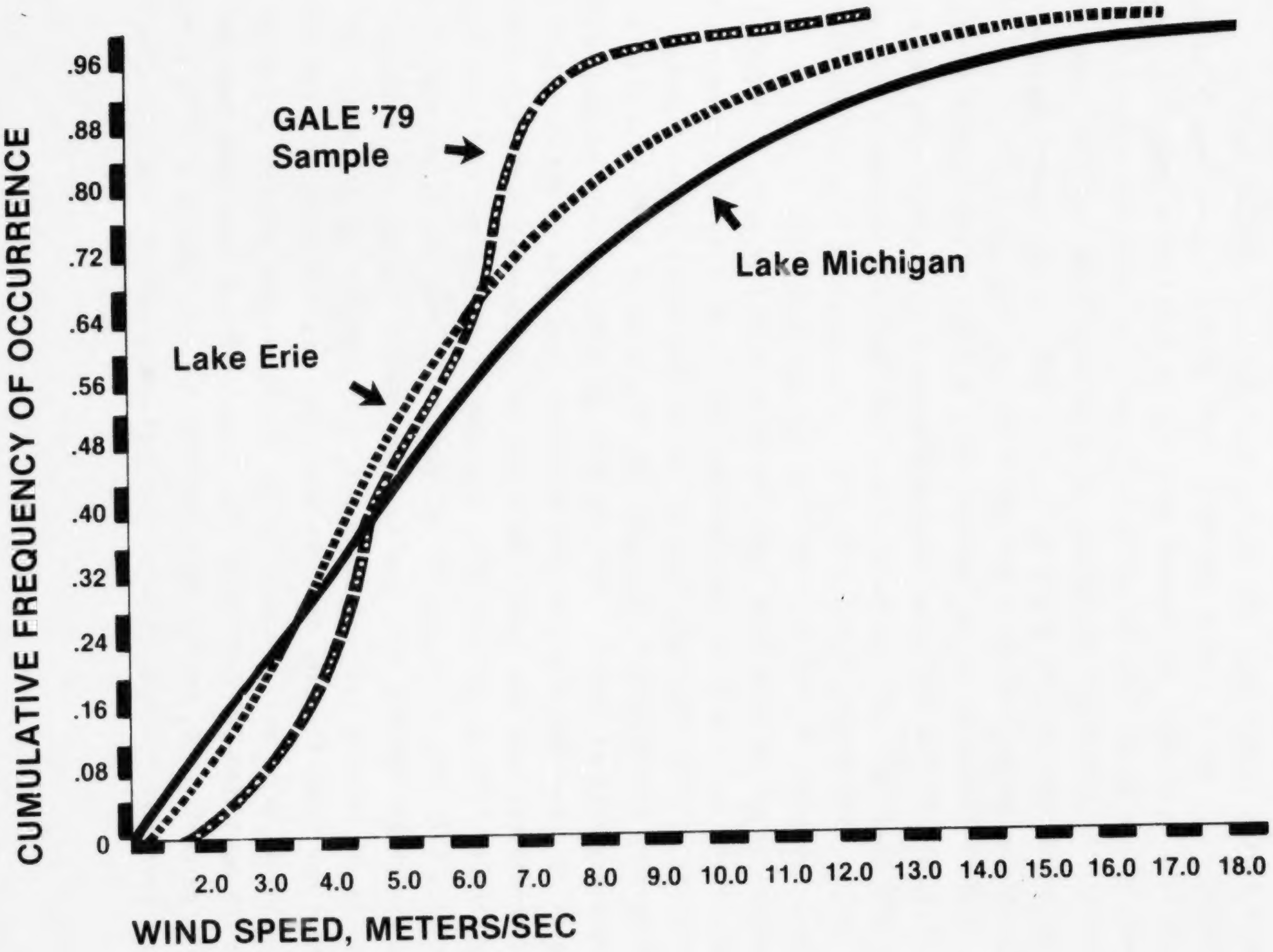

Figure 10. Cumulative Frequency Plot of Ship-sampled and Lakes Erie and Michigan Climatological Wind Speed Conditions.

5.2 AEROSOL CHARACTERISTICS AND THE ESTIMATION OF ATMOSPHERIC DRY LOADING

Even though meteorological conditions were not representative of Lake Erie's climatology, aerosol characteristics may have been so. It was, however, noted at the close of Section 4 that the Cleveland source area (southwest wind direction sector) was severely under-represented. This raises doubts about the representativeness of aerosol data in Tables 1, 2, and 3. Since the major anthropogenic source area (Cleveland) was lacking in its contribution and since no other anthropogenic sources were within 40 km it is reasonable to expect the aerosol character to be similar to continental background or rural conditions. Indeed, elemental concentrations in Table 2 are quite low. Yet, the enrichment factors for Cu and Zn are high relative to those over Lake Michigan.

Rahn (1976) has suggested that rural and remote continental aerosol should all display the same relative elemental proportions. Peirson et al. (1974) observed such a uniformity at eight locations throughout the United Kingdom. Stolzenburg and Andren (1981) also observed this uniformity in rural areas of the United States. It was concluded that a close comparison of the Lake Erie, Lake Michigan, and other aerosol elemental data bases would help resolve the question of Lake Erie aerosol representativeness. This effort has resulted in the Appendix B paper--Chemical Uniformity of Atmospheric Aerosols: Its Violation at a Mid-Lake Erie Site. Close scrutiny of Tables 1 and 2 of this Appendix (and the related text) makes it clear that the Lake Erie elemental data base is not representative of conditions over the lake. The violation of chemical uniformity (observed by others: Peirson et al., 1974; Stolzenburg and Andren, 1981; and King et al., 1976 even in Cleveland) by, especially, the low Pb and high Cu and Zn enrichment factors over Lake Erie make this a dubious data base to use in the binning analysis described in Section 3.1 (equation 2). On the other hand, the Lake Michigan data base fits the chemical uniformity hypothesis quite well, supporting its use in binning analyses performed in the past (EPA-905/4-79-016). The Appendix B paper suggests that the high percentage SO_4 aerosol mass contribution over Lake Erie (27%) versus that over Lake Michigan (12%) may have played a role in this violation of the chemical uniformity hypothesis. In any event, a severely restricted use of the binning analysis must be considered in arriving at Lake Erie atmospheric dry loading estimates.

Before taking a close look at the Lake Erie loading estimates, it should be noted that all elemental concentration data were corrected for two types of sampling losses: a) cascade impactor loss of particulate matter to the walls of the impactor (Specified only in the last few years); and b) aerosol pass-through loss past the Misco backup filter. The former has been identified by the cascade impactor manufacturer (Sierra Inc.) as 5 to 10%. Since only two stages of the maximum five-stage impactor were used in Lake Erie (and Lake Michigan) sampling a value of 5% loss, equally shared by the two stages' aerosol mass has been applied to the data in Tables 2 and 3. The second correction--aerosol pass-through loss--was determined as a part of this Lake Erie Grant research. Results are fully described in Appendix C. Overall mean percentage pass-through loss was found to be 38,32 and 11% for Pb, Zn, and Fe, respectively. Given the fine/coarse ratio (F/C) of these three elements and the F/C of other elements (Table 2) a correction of 10-40% (dependent upon element) was applied to the fine fraction mass determined by ICAP analysis. One final correction--to reiterate--has been applied to the comparative presentation of Lakes Erie and Michigan dry loading estimates in the Executive Summary; the deposition velocity parameterization at the end of Section 4. Thus, Lake Michigan loading estimates presented in this document are about one-half those presented in the Lake Michigan final report (EPA-905/4-79-016).

As stated in the Executive Summary of this document, use of the binning analysis with Lake Erie data results in very large uncertainty loading estimates--at least an order of magnitude. The lack of representativeness in aerosol elemental concentrations and meteorological data in combination with the still quite ill-determined deposition velocity causes one to view the Lake Erie loading estimates "with some skepticism." Given the poor representation of high wind speeds and certain wind directions, the comparison of Lake Erie loading figures with Lake Michigan loading figures is not very meaningful; and it is meaningless to attempt any extrapolation of the two lakes' loadings to others of the Great Lakes.

Cleveland source area) wind direction sector was very severely under-represented (11% of ship sampling time as opposed to 20% of the climatologically average year.) The same statistics when applied to earlier Lake Michigan data base give a much higher concordance between that ship sampling data base and the Lake Michigan climatology--except that > 9 m s^{-1} wind speeds are still under-represented. (A cautionary remark about probabilities calculated by the chi-square test: too few filter sets (28) are available to properly apply the chi-square test. The probabilities stated above would likely increase had a larger data base been obtained. Nonetheless, the stated probabilities, being so very low, are a strong indication of the poor representation.)

The mesoscale lake breeze effect on meteorological conditions during ship sampling was much less pronounced than during Lake Michigan sampling. Only during four of 28 data sets were back-trajectories not drawn due to complexities caused primarily by the lake breeze effect. As a result, further analysis of the Lake Michigan lake breeze periods culminated in the Appendix A Paper, Lake Breeze Effects on Particle Size Spectra and Sulfate Concentration Over Lake Michigan, which shows that aerosol sulfate may increase as a percentage of total aerosol mass while air parcels traverse the lake breeze cell.

A "funnelling effect" over Lake Erie was not previously observed over Lake Michigan. This effect over Lake Erie is seen as a funnelling of the wind flow over the western end of the Lake causing a turning of the wind in a direction in accordance with the shape of the Lake. Since the Lake is shaped such that the west end faces the northwest direction and curves around towards the northeast, the prevailing wind flow is observed as following this shape. This over water flow is often seen as being much stronger (about 2-3 times faster) than the overland surface velocities. It has been noted during the funnelling effect that the wind velocities were stronger on the windward side of the Lake than on the leeward side. The above was observed to occur predominantly with southerly flows. The speeding up of winds over the lake and longer traverse over water caused by the funnelling effect should enhance pollutant fluxes to Lake Erie.

Yet, there is meaning in comparing the relative loadings--one element to another. Or, still better, there is meaning in considering the relative contribution of natural and anthropogenic sources to the aerosol elemental concentrations observed over Lake Erie and Lake Michigan.

5.3 NATURAL AND ANTHROPOGENIC SOURCE CONTRIBUTIONS TO GREAT LAKES ATMOSPHERIC DRY LOADING AND THE FUTURE OF ATMOSPHERIC LOADING ESTIMATES

Given the difficulties encountered in the estimation of atmospheric dry loading to date it may be more fruitful to pursue a different interpretive path. Recent developments in receptor-oriented multivariate statistical analysis (Gordon, 1980; Cooper and Watson, 1980) have resulted in a powerful technique to quantify the contribution of several aerosol source types to the aerosol elemental concentrations observed at the midlake receptor sites. This technique may be labelled chemical mass balance if a sufficiently large percentage of the aerosol mass has been chemically characterized. In the case of the Lake Erie and Lake Michigan data bases less than one-third of the aerosol mass has been characterized by elemental, sulfate ($SO_4^=$) and nitrate (NO_3^-) analyses. Thus, a chemical element balance (CEB) approach was considered. Appendix D, Chemical Elements in Atmospheric Aerosol over Southern Lake Michigan: the Contribution of the Lake Source, is the result of elemental balance across seven source types as applied to the 1979 crib site data base. The crib site data base was chosen for CEB application for two reasons: 1) this data base is smaller than the mid-Lake Michigan data base, making this first CEB application easier from a computational standpoint; 2) the highest quality chemical analyses appear to have been performed on these '79 crib samples. From a long-term Great Lakes research perspective the crib site CEB results must be considered preliminary. Nonetheless, some very interesting (preliminary) outcomes may be found in the Appendix D paper. Of greatest interest is the somewhat tentative indication of a substantial lake aerosol source--both fine fraction (diameter, $D < 1$ μm) and coarse fraction ($D > 1$ μm). See Tables VII and VIII as well as related text of Appendix D.

A preliminary analysis of the USEPA Great Lakes Atmospheric Deposition network data suggests the presence of a lake aerosol source (Lueck and Sievering, 1981). Figure 7, an example ASAS number distribution plot, had shown a bimodality suggesting the presence of a lake aerosol source with a mean diameter of ~ 1 μm. This supports the CEB analysis result above. A fine/coarse fraction comparison of midlake to crib site data on Lake Michigan (Table IV of Appendix D) does not violate this outcome, although it does show an enhanced Mg and Ca concentration in midlake large aerosol compared to the crib site. (Note: the SO_4 and Pb fine/coarse fraction comparison [again see Table IV of Appendix D] indicates an enhanced midlake fine fraction. This is probably due to the coagulation of aerosol less than 0.1 μm which cause the crib site fine/coarse fractions to increase at midlake.)

The magnitude of the lake source--both fine and coarse fraction--indicated by CEB analysis is from one-half to twice the soil source. The fine fraction lake source was found to about equal the sum of anthropogenic source contributions to total fine fraction aerosol mass. Of course, the lake source does not contribute significantly to specific anthropogenic pollutants such as Pb, Zn, and Cu. Further, it should be noted that fugitive dust sources were not considered in the CEB analysis. In the Chicago/Gary area, fugitive dust area sources contribute about equally with anthropogenic point sources to the suspended particulate matter (B. Bolka, 1982). However, these fugitive dust sources (primarily highway aerosol and road dust) should not be of a similar chemical constituency as the lake source.

The exercise of using multivariate statistical analysis (here, chemical element balance approach) has proven to be a fruitful one. It appears to have enough merit that its application to the larger mid-Lake Michigan data base is planned among future research activities. In particular, the determination of the relative contribution of several anthropogenic source types to over Great Lakes aerosol mass or of their relative contribution to a particular element's overlake mass concentration would be of special interest to the USEPA. Another look at Table VII of Appendix D shows that a relative contribution of cement manufacturing, steel production, oil burning, automobile exhaust and coal burning to crib site aerosol mass concentration has been obtained. If CEB analysis were applied to the larger and isolated (i.e., removed from the immediate vicinity of source types) mid-Lake Michigan data base, the delineation of major anthropogenic source type contributions--

at least one type relative to others--could be specified. This could prove immensely helpful to the USEPA in Great Lakes enforcement strategies.

There is yet another reason for taking this interpretive path: the determination of over water deposition velocities for better than order-of-magnitude Great Lakes loading estimation appears to be unreachable within the next few years. It may be better to apply multivariate statistics to a few Great Lakes pollution data bases in that more fruitful outcomes may be achieved from interpretation of these data bases.

Many difficulties have been encountered with Lake Erie atmospheric dry loading estimation. Yet, it was also noted in the Executive Summary that the single most uncertain factor (overwhelming all others combined) in the loading equation--equation 2 in Section 3.1--still remains the deposition velocity, v_d. As long as this situation remains so, the estimation of atmospheric loadings to the Great Lakes by a product of overlake concentration measurements with v_d must remain at order-of-magnitude uncertainty. The remainder of this section 5.3 will first digress into the alternative method for lake loading estimation--lake mass balance analysis--and then close with a brief discussion of some future needs in v_d measurement research.

Dolan and Bierman (1982) have recently published a good example study of mass balance analysis with regard to Saginaw Bay, Lake Huron. This is one of the few mass balance studies which have included sensitivity analysis of the free parameters in the assumed mass balance model. Of the five free parameters, suspended solids and total metals were most sensitive to variations in the settling velocity within the water column. Changes in this parameter result in solids (and total metals) leaving the water column too soon (increased N) or staying in the water column too long (decreased N). A 50% change in settling velocity caused from 24 to 110% change in Cu, Pb, and Zn Saginaw Bay total metal concentrations. This 24-110% range may be compared to uncertainties in the mass balance model results caused by the atmospheric loading input (fixed) parameter. Dolan and Bierman (1982) used the metals analysis from six bulk samplers (collection on a monthly basis) located at several sites around Saginaw Bay. These bulk samples are known to under-estimate the contribution of dry deposition by 200% to as much as 1000% (Clough, 1973; Ton, Eastman, and Sievering, 1983). Assuming the actual dry deposition loading to Saginaw Bay to be 1/4 to 1/2 that of wet deposition, the uncertainty in the atmospheric loading input parameter is from 50% (200% x 1/4) to 500% (1000% x 1/2). This 50-500% uncertainty in atmospheric loading is to be compared with the 24-110% changes in modeled metals concentrations introduced by the most sensitive mass balance model free parameter. Clearly, the uncertainty in the atmospheric loading component overwhelms all others in the Saginaw Bay metals mass balance model.

A similar--but less detailed--mass balance calculation for Lake Erie was provided by Dr. J.A. Schmidt (private communique, 1983). Estimates of atmospheric, tributary and shoreline erosion inputs (fixed parameters) were compared with sedimentation and outflow to Lake Ontario. Table 5 shows the range in inputs and outputs for Cr, Cu, Pb, and Zn. These ranges are: atmospheric, 7 to 17-fold; tributary, 3 to 8-fold; shoreline erosion, 30% to 2 1/2-fold; sedimentation, 40% to 2-fold; and outflow, less than 2-fold. These ranges, the result of a literature/data review, clearly show--again--that our knowledge of atmospheric inputs is the weakest. The order-of-magnitude uncertainty in atmospheric inputs, is many-fold larger than all others except the tributary input uncertainty, which is about one-half as large as the atmospheric uncertainty.

Having assured ourselves that a Great Lakes mass balance approach does not significantly increase our understanding of nor reduce uncertainty in the contribution of atmospheric deposition, we can now focus on the last interpretation topic of this report: Future Improvements in Atmospheric Loading Estimates. The last portion of Section 4 on deposition velocity (v_d) parameterization suggested that for aerosol of diameter, $D < 1$ μm, $v_d \approx (1/3 \text{ to } 1/2) \cdot \bar{u} \cdot C_{DD}$ and for $D > 1$ μm, $v_d \approx \bar{u} \cdot C_{DD}$. The assumed relative difference by size of 50 to 65% is the result of aerosol profiling field studies on Lake Michigan (Sievering, 1981). This small difference may be contrasted with the at least ten-fold difference in v_d postulated by Slinn and Slinn (1980) for $D = 0.1$ μm versus $D = 1$ μm aerosol. This discrepancy is at the order-of-magnitude level which has plagued the atmospheric dry loading estimates throughout this report. Slinn and Slinn (1980) obtain this very large v_d difference for $D = 0.1$ μm versus $D = 1$ μm aerosol as a (theoretical) result of their consideration of aerosol growth in the high humidity environment near the water's surface. Sievering (1981) observed the only two-fold difference for aerosol of $D = 0.2$ μm versus $D = 2$ μm

Table 5. MASS BALANCE ESTIMATE FOR LAKE ERIE

Inputs

Element	Atmospheric[1,2,3]	Tributary[2,4,5]	Shoreline Erosion[6]
Cr	15-180	500-1800	120-220
Cu	50-350	1000-3000	130-320
Pb	150-2200	800-4800	240-310
Zn	300-5200	1800-14000	390-700

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[2] International Joint Commission, 1969. "Pollution of Lake Erie, Lake Ontario and the International section of the St. Lawrence River: Volume 12--Lake Erie," 316 pp.

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[6] Monteith, T.J. & W.C. Sonzogni, 1976. U.S. Great Lakes Shoreline Erosion. Task D Report, PLUARG.

Outputs

Element	Sedimentation[7,8,9]	Outflow[10]
Cr	2300-3600	2500
Cu	1700-2700	1000-1800*
Pb	4500-9600	700
Zn	5100-8100	1800

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[10] International Joint Commission, 1978. "Environmental Management Strategy for the Great Lakes System," final report from PLUARG, 115 pp.

*Estimated from Lake Michigan trace metal data and Lake Erie river data.

aerosol considering a small number--13--profiles obtained during moderate wind speed conditions. Thus, a question lingers as to whether the two-fold difference is truly representative (Hicks and Williams, 1980). Yet, the mechanism of surface roughness (and its variation) with roughness element protrusions acting as aerosol collection sites was not considered by Slinn and Slinn (1980). It was considered by Williams (1981) in "A Model for the Dry Deposition of Particles to Natural Water Surfaces." The model is one with a broken surface resistance applied to a percentage of the water's surface area based on oceanic observations by Wu (1979). The equivalent deposition velocity (v_d)--at the small percentage of water's surface which is estimated to be broken--is assumed to be a constant value, either 1, 10, 100, or 1000 cm s^{-1}. Williams suggests the 10 cm s^{-1} value as most probable, but acknowledges that we only know that "broken surface transfer is more efficient than turbulent transfer ($v_d \sim 1$ cm s^{-1})" and that the broken surface deposition velocity is not a constant across the broken surface area. Further, Williams (1981) notes, "In the future, careful measurements of deposition velocity under a wide range of wind speeds and particle sizes should yield estimates of the value of this parameter [broken surface v_d]. Until then we must make the assumption that the broken surface transfer is a constant. Therefore, the effect on deposition by the broken surface is solely contained in the fractional surface area that becomes broken."

A major problem with the Williams model is its steady state character. The assumptions of a constant flux layer as well as constant broken surface deposition velocity allows one to mathemically model air-water aerosol transfer--but too simplistically. Observation of meteorological and wave dynamics at the air-water interface of the Great Lakes should cause any careful observer to denounce steady state modeling as too simplistic and unrealistic. Models such as that of Williams serve a very useful purpose in pointing out areas for further research as he states above. However, the dynamics at the real air-water interface suggest that the actual aerosol deposition is greater than modeling results would have us believe. Enhanced deposition due to the "young wave" phenomenon referred to at the end of Section 4 is to be expected. That discussion noted the likelihood that the developing wave condition causes an increased turbulent transfer.

Thus, a greater effect of the "young wave" phenomenon on small aerosol is to be expected--possibly much greater. Indeed, the Appendix E paper, Some Effects of Wind-Shift on Over-Lake Turbulence and Aerosol Deposition, shows that wind shifts are associated with depletion of near-surface aerosol mass and with departures from isotropy. Turbulence in the high frequency range is known to normally have a ratio of vertical velocity spectra to longitudinal velocity spectra of 4/3 in the isotropic, inertial subrange. Departures from isotropy caused by enhanced energy in the vertical velocity spectra were strongly correlated with a "windshiftiness" parameter (see Table 2 of Appendix E), the rank correlation coefficient being 0.925 (allowing one to reject the hypothesis of zero correlation at better than the one percent level). The fact that aircraft measured near-surface aerosol mass decreased in conjunction with these isotropy departures as well is supporting evidence for the hypothesis that the non-steady state dynamics at the air-water interface may enhance the deposition of, especially, small aerosol. The above discrepancy between modeled ten-fold and field observed two-fold differences in large ($D > 1$ μm) versus small ($D < 1$ μm) aerosol deposition may, then, be attributed to models (to date) not accounting for the non-steady state mechanisms of aerosol deposition at the air-water interface.

A countervailing argument may, however, also be presented. The mechanism of aerosol resuspension from the water's surface is known to be a contributor to large aerosol mass above the ocean's surface (see, for example, Cipriano and Blanchard, 1981). Recently, Sievering, Eastman and Schmidt (1982) have observed that resuspension may also contribute to small aerosol mass above the ocean's surface (at 6-m height). If large aerosol resuspension is more significant over Great Lakes' waters--as it is generally considered to be over the oceans, then the large aerosol downflux gradients observed over Lake Michigan would have been more reduced by resuspension than would those for small aerosol. Resuspension introduces an upflux lake source gradient which was, in fact, observed on more than one occasion during the profiling measurements on Lake Michigan (Sievering, 1981). The large aerosol mode in Figure 7 may again be thought to be that elusive lake source aerosol. The important point here is that the only two-fold difference observed in large (D < 1 μm) versus small (D < 1 μm) aerosol deposition may be attributed more to resuspension of large lake-derived aerosol. Thus, it is quite possible that neither the field observed two-fold nor modeled ten-fold difference in large vs. small aerosol deposition are to be accepted. The answer may well lie in between these two extremes. Knowledge of the correct answer is extremely important since the magnitude of pollutant aerosol deposition is highly dependent upon this answer.

Recently El-Shoboksky (1983) found, for rough versus smooth pipe flow, an eight- to thirty-fold increase in v_d for 1 μm diameter particles. Experimental conditions included average roughness element heights of 7 μm (pipe diameter was 8 mm), a Reynolds number of 10^4 and friction velocity of 120 cm s^{-1}. Although turbulence characteristics were unrealistically high (for ambient atmosphere conditions) the small roughness elements and steady state character were also somewhat unrealistic. These laboratory results certainly support the parameterization of small difference between large and small aerosol deposition.

It must be concluded that "careful measurements of deposition velocity under a winde range of wind speeds and particle sizes: and at the (actual) Great Lakes air-water interface is a future research necessity. For the purposes of Great Lakes research, species specific measurements are also a necessity. Pollutant species, e.g., Cd, Cu, Pb, and Zn, may be observed to be depositing into the Great Lakes at the same time that Ca, Mg, and other potentially lake-derived elements are emanating from the lakes' surfaces (see Section 4.1 and 5.2 on the evidence for a lake source). Of the presently available deposition velocity measurement methods, i.e., eddy flux, eddy accumulation, variance and gradient techniques, the most promising for species specific measurement is the gradient technique. Although difficult to utilize over water this technique is no more difficult, logistically, than the others mentioned; however, a less direct measurement of v_d is obtained and both vertical temperature and wind speed gradients should be monitored in conjunction with the aerosol gradient.

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APPENDIX A

LAKE BREEZE EFFECTS ON
PARTICLE SIZE SPECTRA AND SULFATE CONCENTRATION
OVER LAKE MICHIGAN

by

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ABSTRACT

Aircraft flights over southern Lake Michigan in September of 1977 and May of 1978 conducted during which meterological and size-distributed particle data were gathered. An anomalous local maximum of the particle distribution in the 0.3 - 0.4 μm diameter range occurred on those days during which a lake breeze took place. This effect contributes more than 20 percent increase in the particle volume across the 0.2 - 0.5 μm diameter range. Evidence is presented suggesting that SO_2 gas to sulfate particle conversion may be responsible.

1. Introduction

The distribution by size of atmospheric particles is an important variable in the various aspects of air pollution, particularly in the lowest layers of the atmosphere (Mészáros, 1977). The size distribution of sulfate particles is particularly important in the investigation of acid rain in the vicinity of and over the Great Lakes. It has only recently been realized, beginning with the work of Winchester and Nifong (1972), that dry deposition of atmospheric particles constitutes a major source of certain pollutants to large water bodies such as Lake Michigan. Thus, until the last decade, there had been few in situ investigations of particle characteristics over water.

Early measurements of size spectra over natural water surfaces were reported by Junge (1972), who observed the typical -3 power law distribution. Bridgeman (1979) has measured particle size spectra over the midwest. Measurements over Lake Michigan were not the primary focus of that study, but one over-lake flight was made using instruments very similar to those used in this study. Extinction coefficients indicated the presence of extremely clean air and bore some resemblance to rural air extinction coefficients. Most evidence suggests that in the range $0.1 <$ diameter $(d) < 10\ \mu m$, the number distribution is bimodal with maxima around $d = 0.1 - 0.3\ \mu m$ and $d = 5.0 - 8.0\ \mu m$ (Whitby, 1973). But, as pointed out by Whitby (1978), this modality is only marginally visible in the number distribution, and is most evident in the surface area and volume distributions. In connection with the Great Lakes Atmospheric Loading Experiment (GALE), measurements of size spectra, along with other data, were gathered aboard an airborne platform in 1977 and 1978 over the southern basin of Lake Michigan.

2. Instrumentation

Measurements were taken aboard a Beechcraft Queen Air aircraft provided by the Research Aviation Facility of the National Center for Atmospheric Research. The aircraft departed from Midway airport and, upon reaching the lake, proceeded at a low altitude (usually 30 m) to the midlake sampling site, 87° 00´ W, 42° 00´ N. Vertical soundings were taken in a square spiral "box" pattern over this site, over a point halfway to shore, 87° 15´ W, 41° 52´ N (referred to as the halfway point) and, in 1978, over a near-shore site, a City of Chicago water intake crib, 87° 32´ W, 41° 47´ N (see Figure 1.). The lowest data were taken at an altitude of 15 m and the soundings extended through about 2000 m. Flight times were approximately 0700-0900 CDT, 1100-1400 CDT, and occasionally 1600-1800 CDT during September 26-30 of 1977 and May 17, 19, 22-24, and 26 of 1978.

Particle size spectra were obtained from the Active Scattering Aerosol Spectrometer (ASAS) manufactured by Particle Measuring Systems, Boulder, Colorado. The instrument measures light scattering internal to the cavity of a He-Ne laser. By a system of precision optics and photomultipliers, the absolute number of particles in each of 60 size channels is recorded. It is described by Schuster and Knollenberg (1972). The instrument used in 1977 gathered data in the range $0.23 < d < 30.0$ μm. Ambient air was drawn through an approximately isokinetic sampler (see de Pena, et al., 1975 for description) and transmitted along a length of copper tubing to the intake port of the ASAS. Intake was flow-controlled using aircraft Venturis to produce an inflight sampling rate of 0.28 ± 0.20 cm^3 sec^{-1}. The number of counts in each of the 60 size channels, along with various meteorological data were recorded each second onto magnetic tape by the Aircraft Recording Instrument System (Glaser, 1973). Location was determined by an inertial navigation system. Height above 500 m was determined by a pressure altimeter, and below 300 m by a radio altimeter. A weighted average of the values from these two instruments was used between 300 m and 500 m.

During 1978 a slightly different configuration was used. The ASAS used during this period gathered data in the range $0.11 < d < 3.0$ μm and the copper tubing was somewhat longer and was heated to significantly reduce water vapor contribution to ASAS number counts. Interpretation was aided by National Weather Service surface and upper air data. Surface high volume filter, bulk water and meteorological data were also gathered in connection with the GALE at mid-Lake Michigan in 1977 and at the near-shore site in 1978 (Sievering, et al., 1979).

3. Calculation of Particle Size Spectra

The instrumentation used and the experimental setup produced several consequences which made the calculation of the size spectra less than straightforward. It was feared that the length of copper tubing used to transmit the air sample would cause some loss of measured aerosol counts. To investigate this, the original tubing from the two aircraft configurations was used to sample air which was drawn through the approximately isokinetic sampler in a wind tunnel at Particle Measuring Systems in Boulder, Colorado. The spectra thus obtained were compared with spectra obtained without the copper tubing and the loss of aerosol as a function of size was calculated. In the spectra that follow, the raw number count was multiplied by the factor required to compensate for this estimated loss. These correction factors are shown in Figure 2. Since the ambient air in Boulder, Colorado was used to obtain these curves their applicability is uncertain, but it should be noted that the correction factor for particles with diameters less than 0.5 μm is quite small. Our attention was principally directed to this size range.

The 60 sampling channels are grouped into four slightly overlapping "size ranges" of 15 channels each. Because of the manner of operation of the ASAS, it is possible for a size range to systematically measure number counts which are higher or lower than neighboring or overlapping size ranges. This was observed to occur in the larger of the two size ranges in 1977 and the second smallest of the four size ranges in 1978. The signal-to-noise ratio is higher for the larger-radius channels in any of these size ranges, so the groups with anomalously high readings were empirically matched with the overlapping larger-radius channels of a neighboring size range. As a result, number counts in the anomalous range were multiplied by 0.08 for the 1977 data and 0.33 for the 1978 data to bring it roughly in line with neighboring ranges. Because of this, while relative differences between individual samples and relative numbers within a group retain their validity, absolute numbers are suspect.

4. Description of Data

Five flights in September of 1977 and seven in May of 1978 were chosen for concentrated study. These flights were selected so as to obtain data from air which had a direct trajectory from an urban area (September) and from air which either clearly underwent lake breeze circulations or from that which did not (May). Table 1 presents certain meteorological parameters measured at the lake's surface during these flights. Temperature difference between 5 m height and the surface was obtained using an infrared thermometer. Distributions of aerosol number were in general unremarkable, following a typical -3 power curve described by Junge. In the range above 2.0 μm diameter, particle counts were too few to accurately locate the large particle size maxima in the bimodal surface and volume distributions. With an exception yet to be discussed the small particle size maxima were near $d = 0.2$ μm. Total particle volume in the range $0.11 < d < 2.0$ μm near the surface was in the range 10 to 20 x 10^{-12} cm^3 cm^{-3} in September, 1977 and 20 to 30 x 10^{-12} cm^3 cm^{-3} in May, 1978. Total particle number counts were 15 to 90 cm^{-3} in September and 200 to 600 cm^{-3} in May.

Three of the May flights (18, 22, and 25) had a spectral anomaly in the form of a local maximum located within the range $0.3 < d < 0.4$ μm. The appearance in the number spectrum is that of a minor "bump" (see Figure 3). This bump represents an increase in the particle number count on the order of 100 cm^{-3}; this is an increase of about 30 percent in the $0.2 < d < 0.5$ μm range over the number of particles counted in this range when the bump is absent (see Figure 3). As mentioned above, this type of local maximum is more obvious in the volume distribution plots. Figure 4 shows the volume distribution corresponding to the number spectrum plot in Figure 3. The Whitby (1978) grand average continental distribution has been forced to fit the small and large particle ends of the distribution for the 1242 - 1245 CDT, 60 m altitude, near-shore data on May 18, 1978. For this case, then, the bump referred to above is evident in the $0.25 < d < 0.5$ μm range. Clearly in this case, and quite often otherwise, the $d \sim 0.4$ μm maximum exceeds the average continental distribution volume maximum at 0.3 μm. The bump invariably represents an increase in particle volume of more than 20 percent in this range. The bump is often quite narrow in range (< 0.2 μm), suggesting a single source for these particles. Since surface area and volume affect the reactivity and the air/water exchange of particles, the anomaly may be of singificance to sulfate formation and particle loading of the lake.

The three flights on which these bumps were observed (May 18, 22, and 25) took place during lake breeze episodes. The aircraft made it possible to directly observe the lake breeze cells (see Figure 5). Backward-in-time trajectories were calculated for all experimental periods by a process described in Sievering, et al. (1980). These trajectories, shown in Figure 6, also support the existence of a lake breeze on May 18, 22, and 25, 1978.

There were some differences in the appearance of the bumps on these three days. On May 22 and May 25, the bumps usually appeared in the range $0.35 < d < 0.45$ μm, but on May 18 the bump also extended below 0.35 μm. The bump was always found in air samples at altitudes of 30 to 60 m above the surface on the three lake breeze days. This seems to indicate that the domain of this anomalous distribution was spatially continuous in near-surface layers. On May 22 the bump was found up to altitudes of 600 m while on May 18 and May 25 it was found at altitudes near to 110 m and a second discrete region was found between 220 and 800 m. The data at higher altitudes is more sparse because of both the flight track and the greater length of constant altitude data needed to obtain statistical significance in particle counts at higher altitudes.

The September flights, in contrast, showed only a half-dozen isolated instances of a local maximum in the $0.35 < d < 0.45$ μm range. This was true despite the fact that all of these September flights occurred when there was a wind directly from the heavily populated area to the west and southwest of the sampling area. That the urban plume was in fact sampled during the September flights is indicated by a time plot of the total aerosol volume detected over the lake (Figure 7). The abrupt increase, if extrapolated back in time using aircraft-measured mean wind speeds, occurred in air that would have left the industrialized western shore of the lake around 0745 to 0815 CDT, just as the rush hour was occurring. The aircraft measurements indicate that the wind direction was steady during the 0730 to 0930 CDT period; i.e., the flow was direct rather than meandering. It appears that advection from an urban area is not sufficient to produce the spectral anomaly by itself.

Surface high volume air samplers equipped with three-stage cascade impactors were in place at a 13 m height above the lake surface at the near-shore crib site during May of 1978. Reliable data were available during only four of the six May flights discussed above, but for these days, the ratio of fine ($d < 1$ μm) to coarse ($d > 2$ μm) particles was larger during the lake breeze events perhaps resulting from greater coarse particle deposition during the long over-lake return fetch. Additionally, it was found that concentrations of Pb, V, Zn, and Cu (metals especially associated with anthropogenic sources) were enhanced on the lake-breeze days (see Sievering and Dolske, 1982). The high volume filters were analyzed for sulfates and phosphates as well as trace metals. The ratio of sulfate to certain of these trace metals and to phosphate is shown in Table 2. These ratios were averaged for the two lake breeze and the two non-lake breeze days. It is evident that in the comparison of at least these four periods, sulfates were strongly enhanced with respect to Pb, Fe, Mn, and P-PO_4 and somewhat enhanced with respect to Zn.

5. Discussion

The appearance of a local maximum of restricted size range in an otherwise ordinary particle spectrum suggests a single source type. Two of these anomalous cases occurred when there was no direct surface trajectory from an urban area, as determined by the back-trajectory analyses referred to above. But on those non-lake breeze days when the analyses indicated either urban or non-urban source regions the anomalies were absent. Thus, the lake breeze is sufficient in some cases to cause an otherwise normal particle distribution to be perturbed. Lyons and Olsson (1973), among others, have pointed out the manner in which a spiral-shaped lake breeze can cause a re-circulation of pollutants carried over the lake by a return flow. These pollutants are then brought back to shore by the surface lake breeze. They mention that a size-sorting of the aerosol was detected, which they attributed to gravitational fallout of larger particles. In the case they reported, this caused an augmentation of the smaller aerosol near the surface, similar to that suggested by the high volume air sampler data of Table 2.

Lyons and Olsson (1972) found that particles in the lake breeze return flow penetrated more than 20 km over-lake in a well-developed lake breeze cell. This would be consistent with the occurrence of the spectral bump found 30 - 50 km from shore.

The fact that the bump was not present after the short (< 2 hr) direct fetch from the Chicago area suggests that the lake breeze itself contains a mechanism for the sulfate enhancement noted above. Particles the size of those in the bump ($0.2 < d < 0.5$ μm) are often associated with the contribution of sulfate particles to the accumulation particle mode (Whitby, 1978). Recent work by McMurry and Wilson (1982) in high humidity environments such as that over Lake Michigan shows that particulate sulfate predominates diameters of 0.3 to 0.5 μm whereas low humidity environments produce sulfate particles less than 0.2 μm. Airborne measurements of particle size distributions in power plant plumes conducted by Hobbs, et al. (1979), indicate that an increase in 0.3 to 0.5 μm diameter particles on the order of 10 to 20 cm^{-3} above ambient concentrations could be expected after a few hours travel time, presumably from gas-to-particle conversion mechanisms. If the percentage increase is applied to the concentration of particles normally present at mid-Lake Michigan in the $0.3 < d < 0.5$ μm range, an increase of 100 cm^{-3} is found which is consistent with the magnitude of the bump described above. It should be noted that an urban plume would afford more particulate surface area for heterogeneous, catalyzed reactions than particles from an isolated power plant plume. Wilson, et al. (1977), have shown that the transformation rate of gaseous sulfur to particulate sulfur was less than 2 percent per hr in the Labadie power plant plume until mixing with the St. Louis urban plume, at which point transformation rates increased to as much as 5 percent per hr.

Lyons (1975) has described the expected range of wind speeds and the extent of a Lake Michigan lake breeze cycle. Using these estimates (which were consistent with the aircraft observations for May 18, 22, and 25) and assuming subsidence to take place about 30 km from shore, a parcel will take 6 to 10 hr to complete a lake breeze cycle. Assuming a mean travel time of 8 hr and a mean SO_2 to SO_4 transformation rate of 2 percent per hr, well over 10 percent of the SO_2 in the Chicago source region will have been transformed to SO_4 upon arrival at the crib site. Direct transport from the urban shoreline to the crib site would produce well less than 1 percent transformation. To complete the SO_2 to SO_4 transformation calculation, the rate at which growth occurs through the particle size spectrum is needed. McMurry and Wilson (1982) show that sulfate particle growth per unit of time Dp/dt) is about 0.02 μm hr^{-1} and that this growth is essentially independent of the initial particle size. A nominal growth time for growth of an additional 0.3 μm in diameter is then about 15 hr. Although this time is about twice as long as the 8 hr mean lake breeze travel time it should be noted that the major Chicago region SO_2 sources are not at the lake's shoreline. These sources, clustered in the vicinity of Joliet, IL, were from 3 to 5 hr removed from the lakeshore (synoptic flow was from the southwest) on the days of interest (Table 1). Further, the 8 hr mean lake breeze travel time would afford an additional sulfate particle growth of 0.1 to 0.2 μm which is exactly the size increment needed to explain the shift in the peak volume distribution from the non-lake breeze cases of 0.2 μm to those lake breeze cases for which the volume peak occurred in the d > 0.3 μm range. It would appear that no anomalous bump appeared during the September flights because of the short travel time from SO_2 sources.

6. Summary

Data gathered over Lake Michigan aboard an aircraft during lake breeze events revealed the occurrence of an anomalous local maximum in the aerosol size distribution in the 0.3 - 0.4 μm diameter particle size range. It is suggested that the re-circulation of the lake breeze provides a material contribution to this anomaly, perhaps providing sufficient time for gas-to-particle conversion to take place. Sulfate fractions appear to be enhanced relative to other chemicals during those lake breeze events sampled.

7. Acknowledgements

Appreciation is extended to the personnel of the Research Aviation Facility and the Computing Facility of the National Center for Atmospheric Research. Assistance in the manual plotting of soundings and trajectories was provided by Mehul Davé, Patric McCoy, and Vic Jensen. Gratitude is expressed to Dixie Butz for her preparation of the manuscript and to John Eastman for his review of a draft.

This work was supported by the U.S. Environmental Protection Agency under grants R00530101 and R00542101.

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Date	Flight Times (CDT)	Height of Thermal Inversion Boundary Layer (m)	5-m Air Temperature Minus Surface Water Temperature (^{0}C)	10-m Height Wind Speed (m/s)	Direction of Backward-in-Time Trajectory ($\pm$ 15^{0}) From Crib Site.
Sept 26	0645 - 0915	None	8.1	8.3	270^{0}
Sept 26	1641 - 1810	None	5.7	6.0	
Sept 27	0639 - 0856	None	7.2	7.4	250^{0}
Sept 27	1120 - 1344	None	6.3	6.5	300^{0}
Sept 27	1636 - 1826	None	5.9	6.1	310^{0}
May 17	1130 - 1411	90 - 260	1.3	3.5	15^{0}
May 18	1130 - 1252	None	6.4	3.0	45^{0}
May 19	1145 - 1313	5 - 10	4.7	3.5	100^{0}
May 22	1133 - 1352	10 - 80	-0.9	2.2	30^{0}
May 24	1130 - 1419	80 - 220	-1.9	1.4	5^{0}
May 25	0715 - 0858	110 - 160	-	-	-
May 25	1145 - 1443	5 - 190	3.2	5.7	90^{0}

Table 1. Meteorological parameters measured during September, 1977 and May, 1978.

	Lake-Breeze Events	Non-Lake-Breeze Events
$[SO_4]/[Pb]$	61	38
$[SO_4]/[Al]$	52	50
$[SO_4]/[Zn]$	94	64
$[SO_4]/[Fe]$	4.2	1.7
$[SO_4]/[Mn]$	67	20
$[SO_4]/[P\text{-}PO_4]$	1605	808

Table 2. Ratio of sulfate mass concentration ($[SO_4]$) to mass concentration of certain trace metals and phosphate for two lake breeze (May 18 and 25) and two non-lake breeze (May 17 and 24) periods.

Figure Captions

1. Location of Sampling sites.
2. Sample tubing loss correction factors as a function of particle diameter.
3. DN/D (log d) as a function of particle diameter. Straight line is -3 Jungian slope, included for reference. 18 May, 1978, 12:42 - 12:45 CDT altitude 60 m, nearshore shows the "bump" whereas 18 May, 1978, 12:12 - 12:19 CDT altitude 1900 m, midlake does not.
4. Same as Figure 3 except the plots are of DV/D (log d) as a function of particle diameter.
5. Wind directions measured by aircraft over Lake Michigan during a lake breeze event.
6. Backward-in-time trajectories on May 18, 22, and 25, 1978.
7. Total particle volume measured in the range $0.11 < d < 2.0$ μm as a function of time.

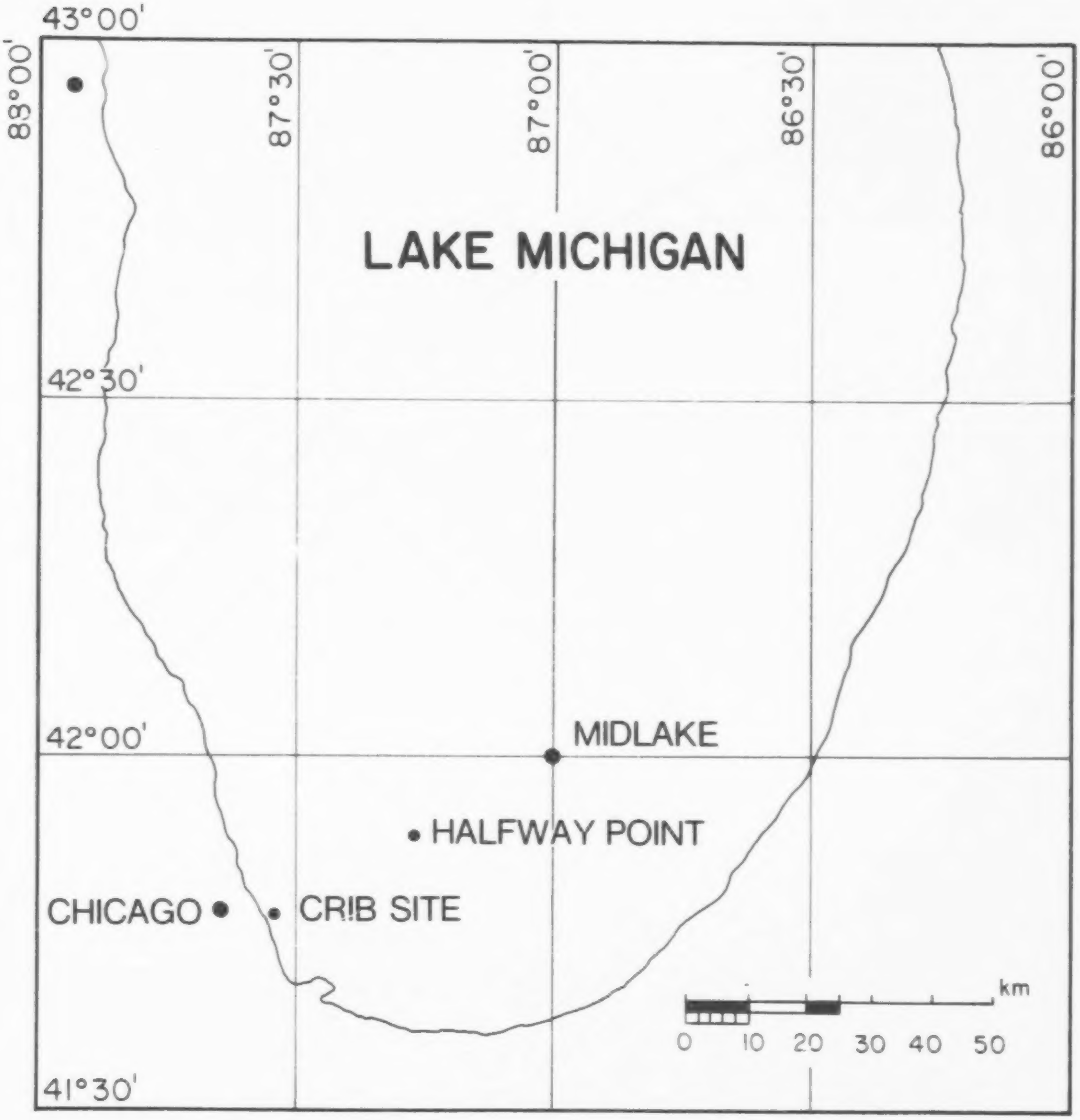
43°00'
88°00'
87°30'
87°00'
86°30'
86°00'
LAKE MICHIGAN
42°30'
42°00'
MIDLAKE
HALFWAY POINT
CHICAGO
CRIB SITE
km
0
10
20
30
40
50
41°30'

Figure 1. Location of sampling sites.

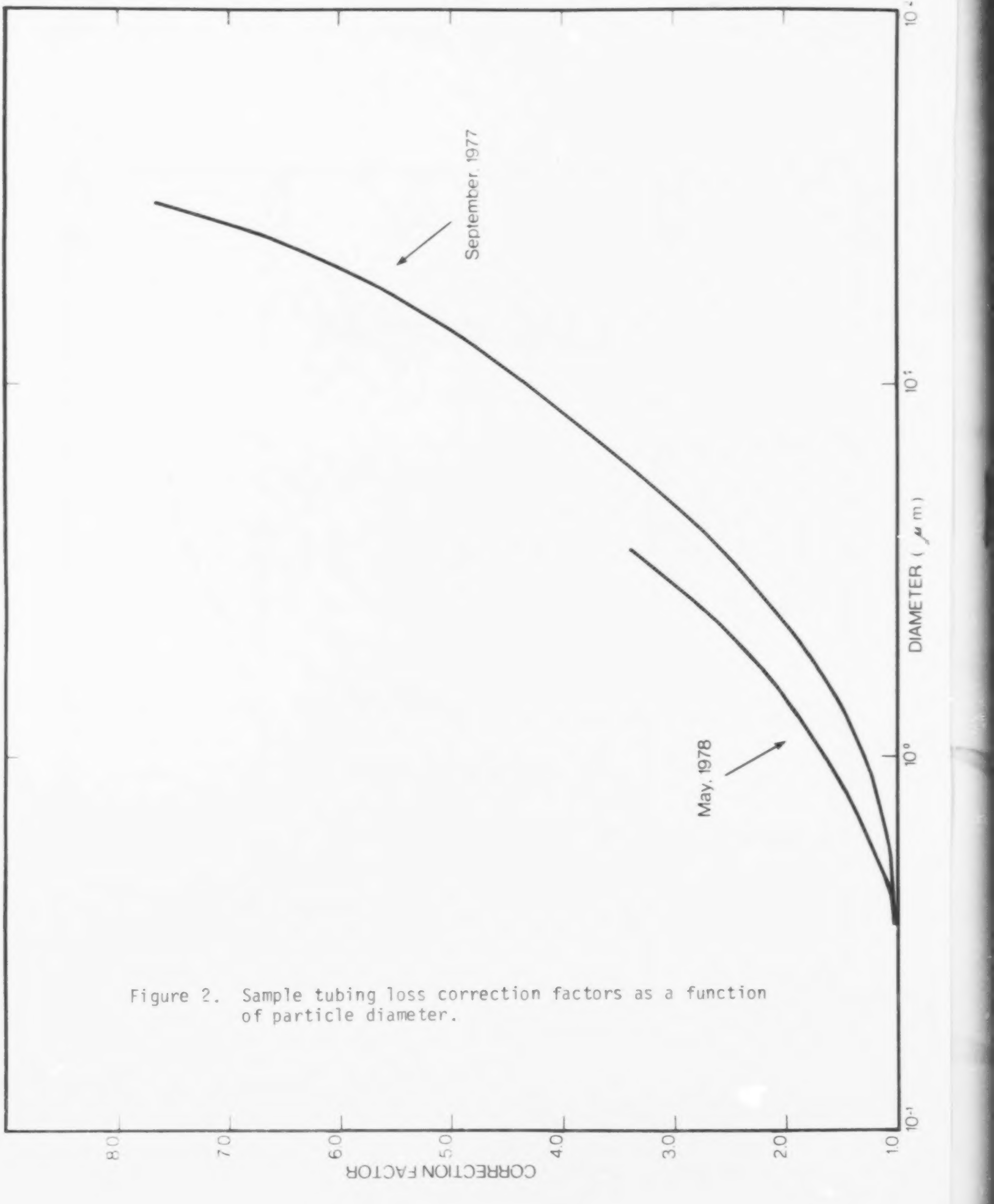

Figure 2. Sample tubing loss correction factors as a function of particle diameter.

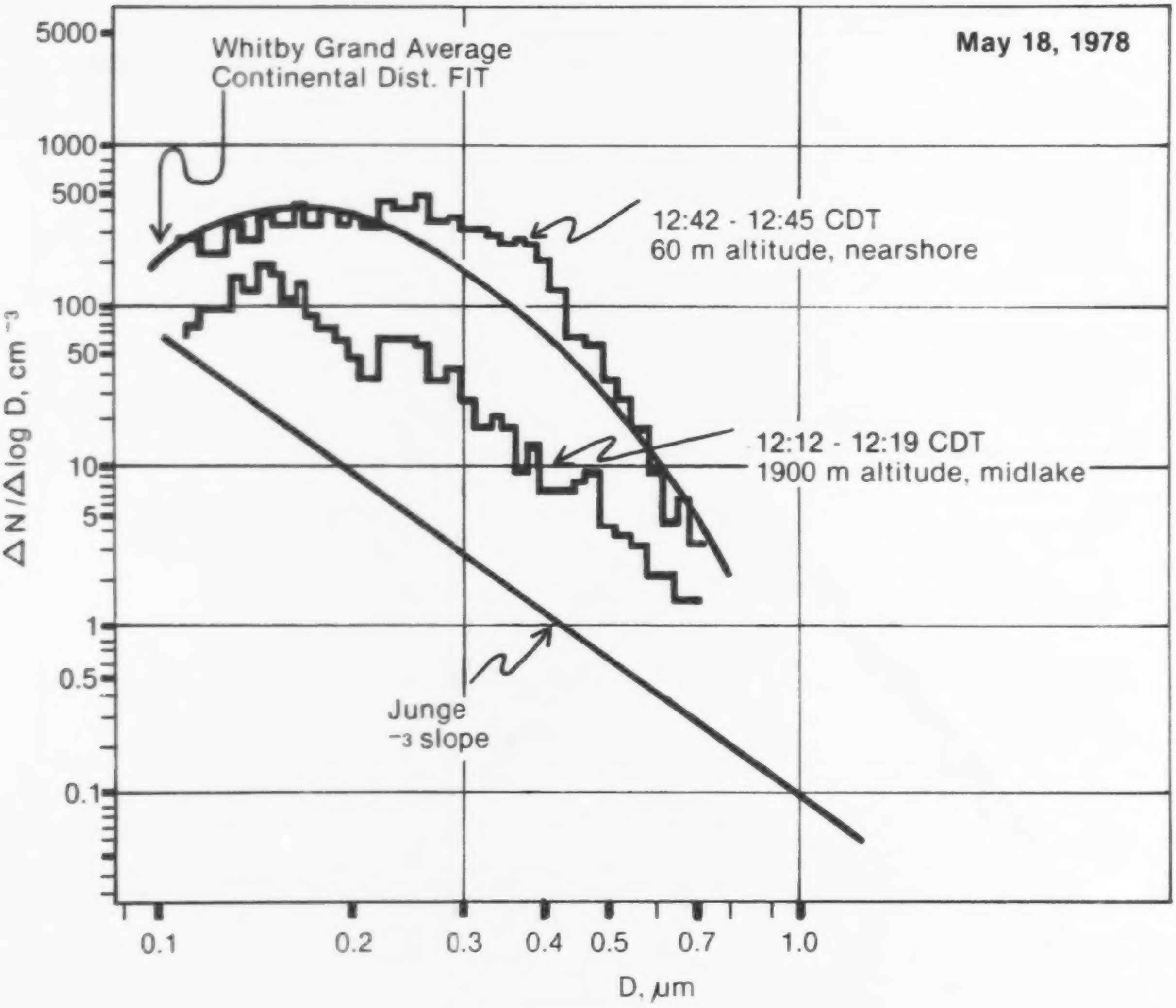

Figure 3. DN/D (log d) as a function of particle diameter. Straight line is -3 Jungian slope, included for reference. 18 May, 1978, 12:42 - 12:45 CDT altitude 60 m, nearshore shows the "bump" whereas 18 May 1978, 12:12 - 12:19 CDT altitude 1900 m, midlake does not.

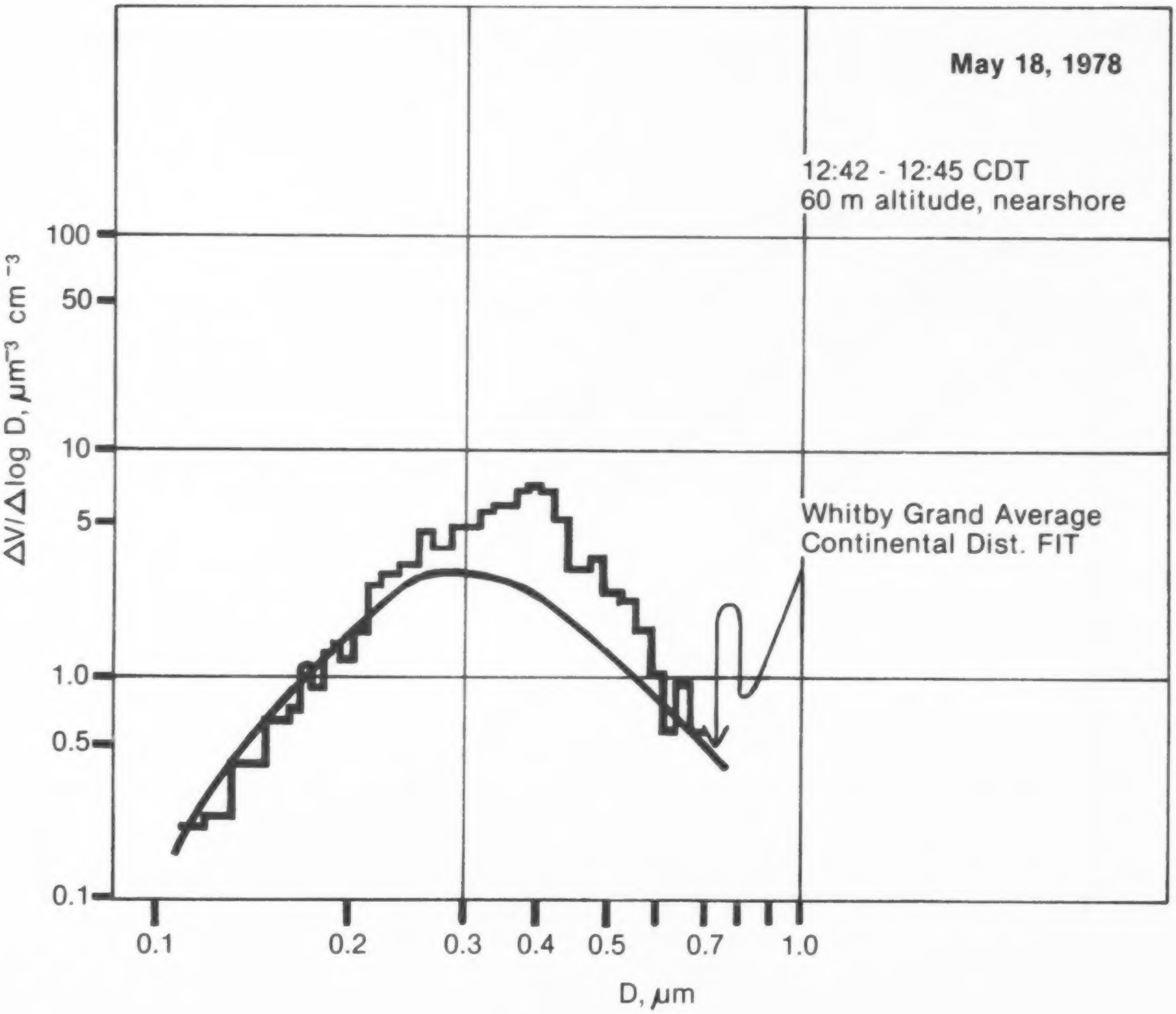

Figure 4. Same as Figure 3 except the plots are of DV/D (log d) as a function of particle diameter.

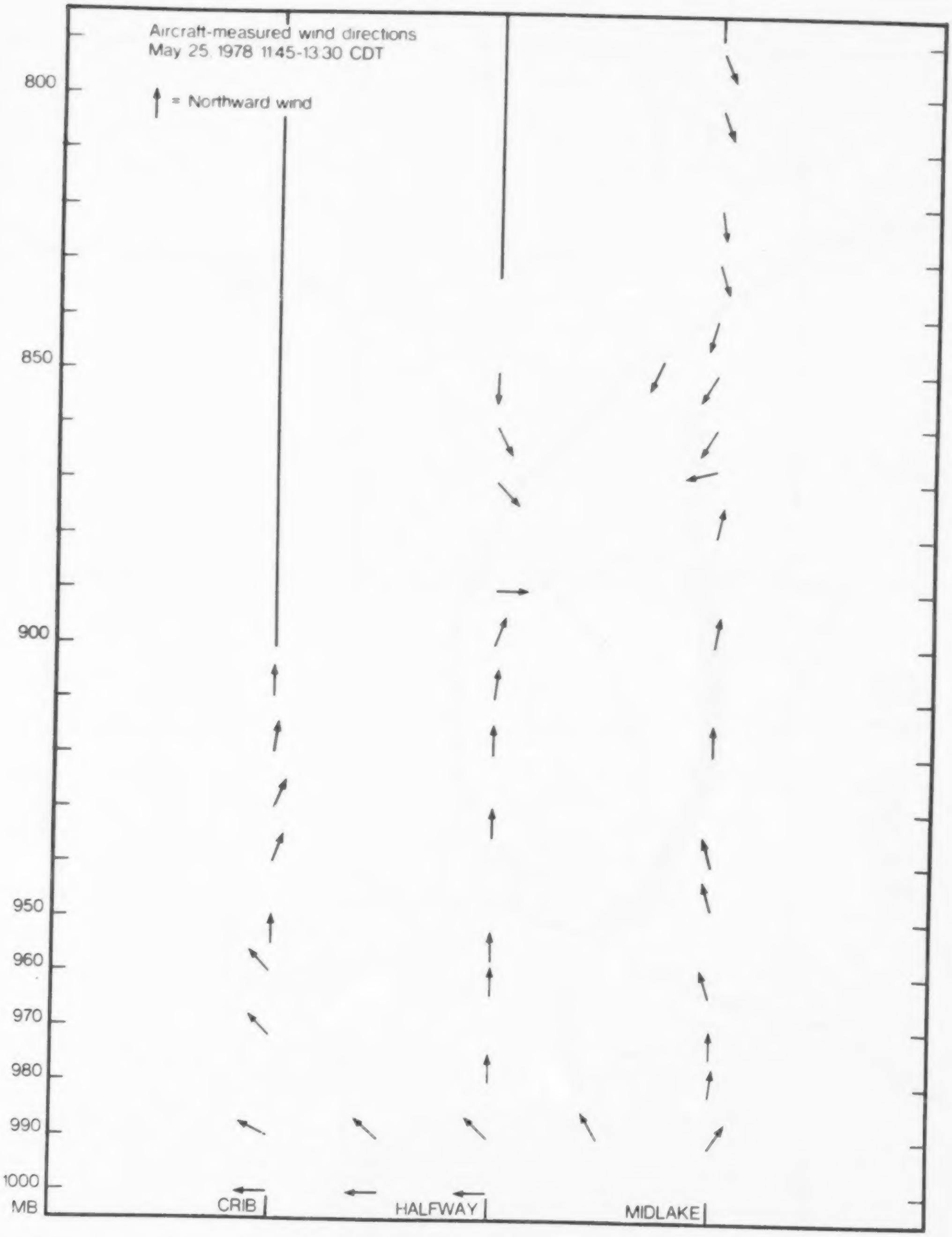

Figure 5. Wind directions measured by aircraft over Lake Michigan during a lake breeze event.

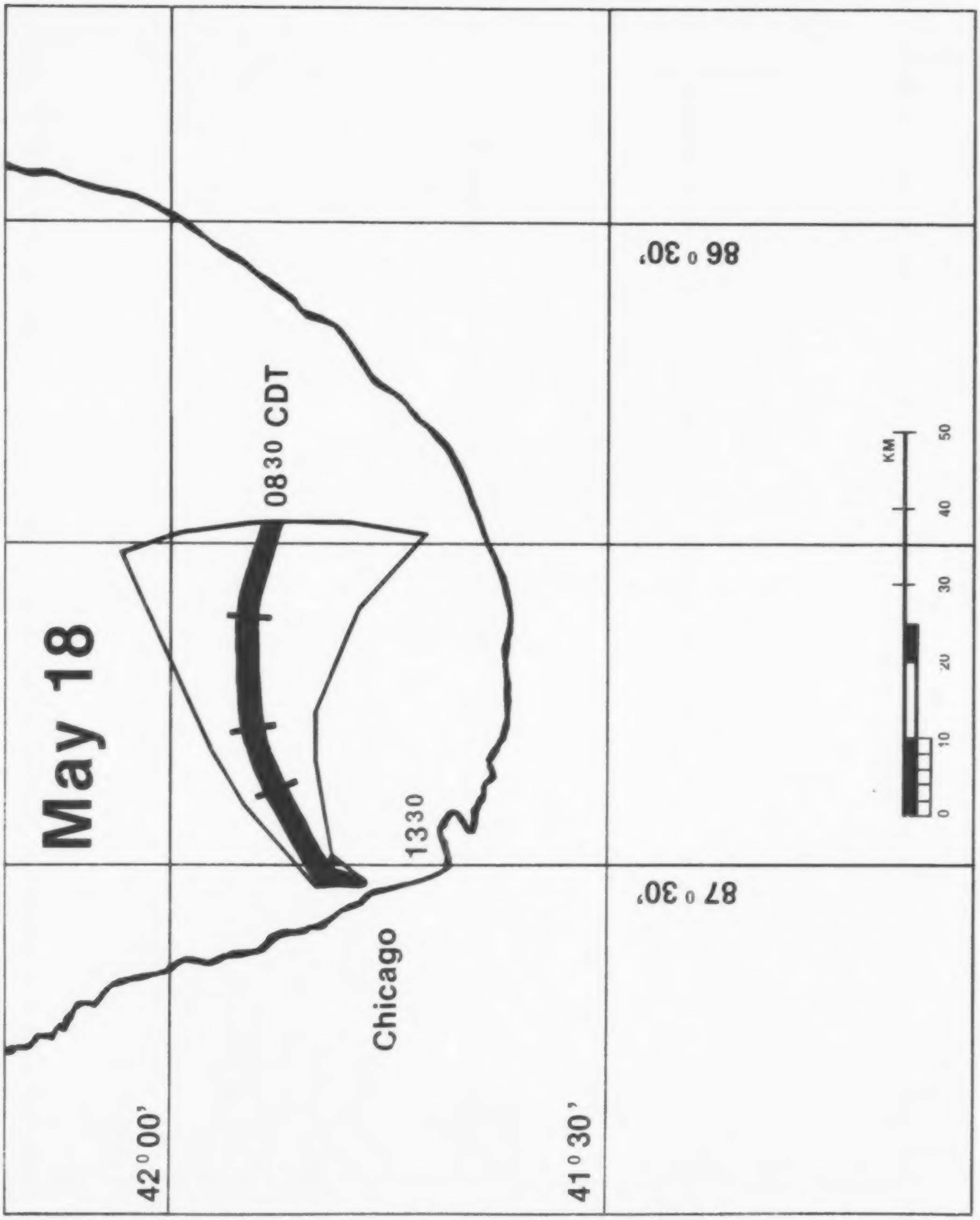
May 18
0830 CDT
1330
Chicago
42°00'
41°30'
86°30'
87°30'
KM
0
10
20
30
40
50

Figure 6a. Backward-in-time trajectories on May 18, 22, and 25, 1978.

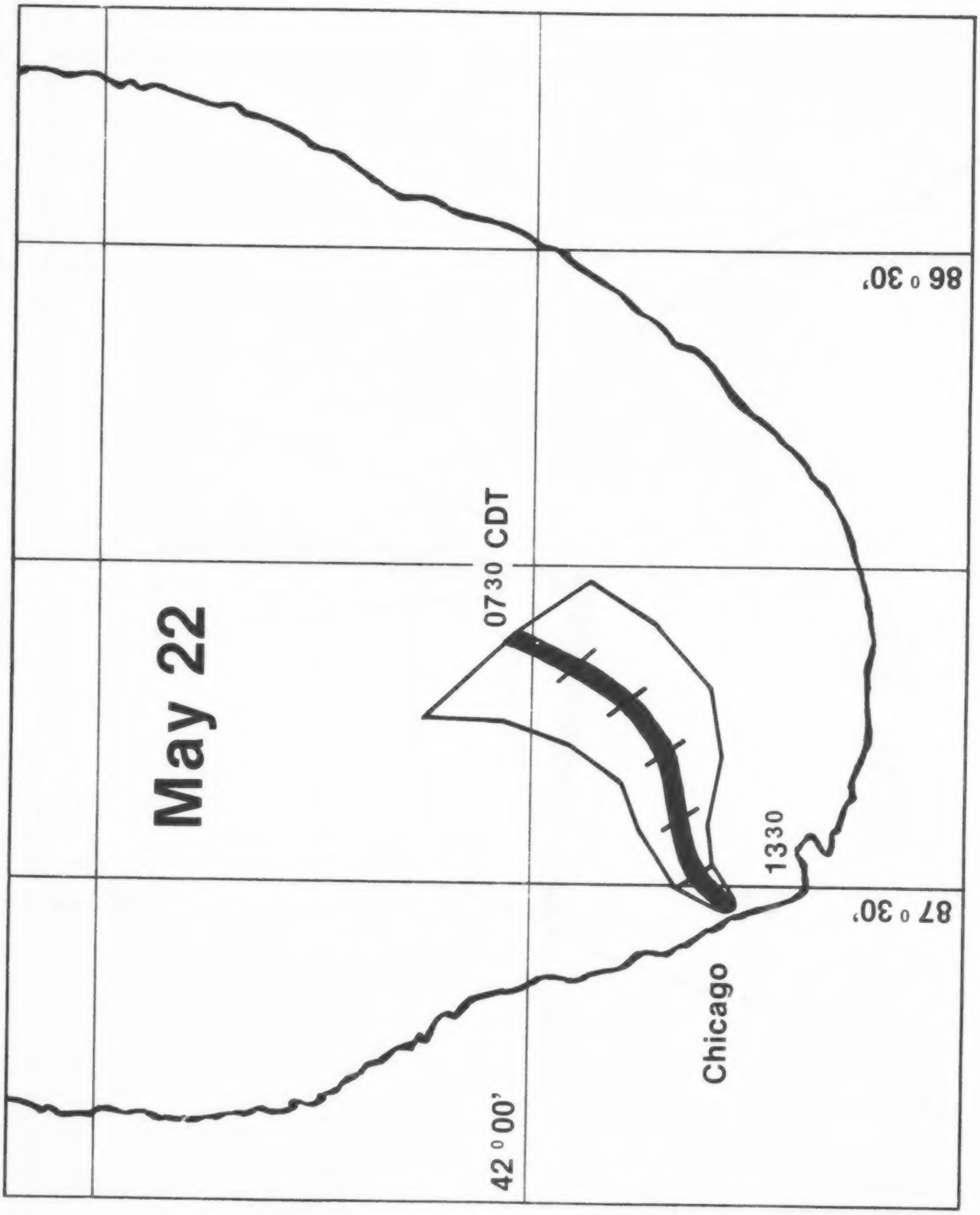
May 22
0730 CDT
1330
Chicago
42°00'
87°30'
86°30'

Figure 6b.

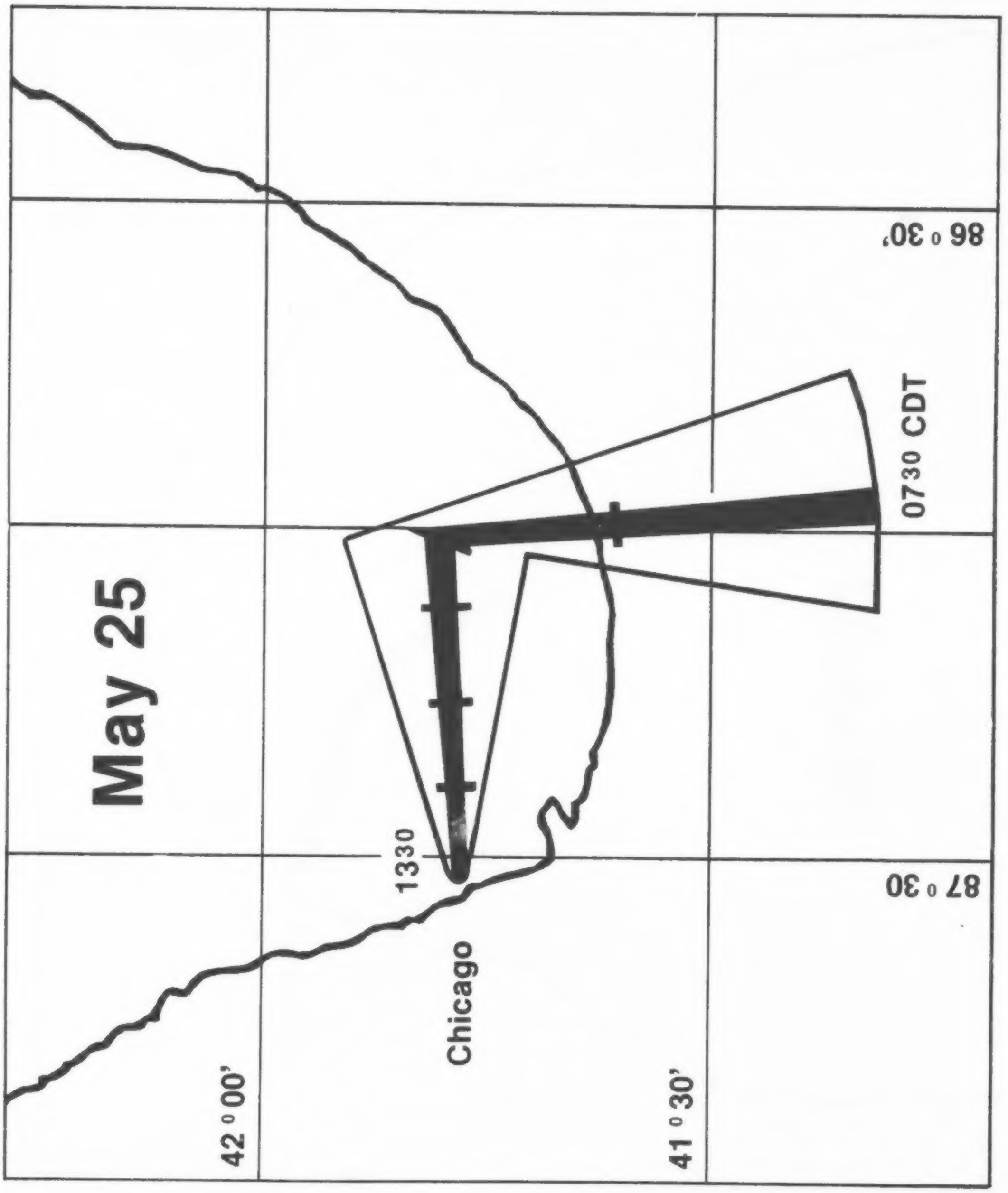
May 25
0730 CDT
1330
Chicago
42° 00'
41° 30'
87° 30
86° 30'

Figure 6c.

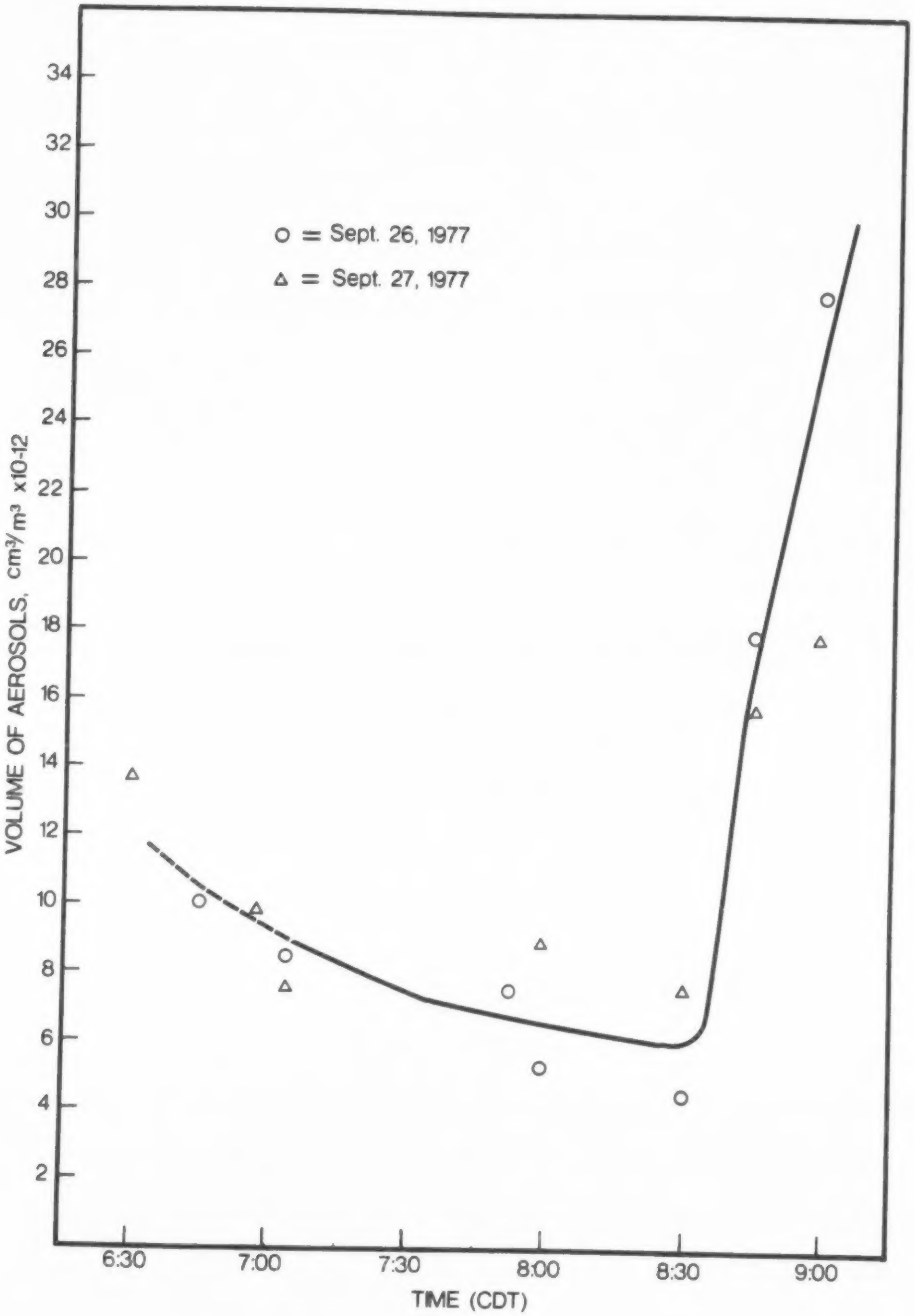

Figure 7. Total particle volume measured in the range $0.11 < d < 2.0$ μm as a function of time.

APPENDIX B

SHORT COMMUNICATION

Chemical Uniformity of Atmospheric Aerosol : Its Violation at a Mid-Lake Erie Site

by

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ABSTRACT

The hypothesis of elemental mass uniformity of continental aerosol is not supported by data collected over the Great Lakes. The twofold higher sulfate concentration in air over Lake Erie compared with that over Lake Michigan may be the dominant factor in producing the compositional nonuniformity.

Peirson et al. (1974) observed a uniformity in the elemental composition of aerosol at eight locations throughout the United Kingdom (UK). Rahn (1976) also noted a striking uniformity in relative elemental composition in remote areas of the world; a similar uniformity has been observed in urban (Israel, 1974) and rural (Stolzenburg and Andren, 1981) areas of the United States. Rahn (1976) has suggested that urban, rural and remote continental aerosol types should all display the same relative proportions of elements. Further, it has been proposed (Stolzenburg and Andren, 1981) that simple dilution can account for most of the observed mass concentration differences between remote continental and urban aerosols. Taken together these arguments will here be called the compositional uniformity hypothesis. This hypothesis is tested below against two aerosol/elemental data bases gathered over the Great Lakes.

Great Lakes sampling and analysis methods have been published previously (Sievering et al., 1980) and will be restated only briefly. Aerosol particulate matter was collected on three-part cellulose filters in a three-stage cascade impactor. This configuration provided fine (diameter, $r < 0.5$ μm) and coarse ($r > 1$ μm) particulate fractions for subsequent elemental mass analysis by inductively coupled argon plasma emission spectroscopy (ICAP) and for sulfate mass analysis by the $BaSO_4$ turbidimetric method. Recovery studies indicate > 90% for all except Al, for which 50-70% recoveries were determined. Al concentrations determined by ICAP were enhanced by a factor of 60% to compensate for poor recovery. Gravimetric analysis for total aerosol mass was also performed. Shipboard sampling was performed using a boom approximately 5 m ahead of the ship's bow; the individual filter sets consisted of air volumes from 200 to 700 m^3. A light-scattering device, the active scattering aerosol spectrometer (ASAS), was used to monitor the in situ number concentration distributions for the 0.1- to 3.5-μm diameter size range. Meteorological parameters were monitored aboard ship. These data, in conjunction with land-based meteorological data, afforded the construction of back-trajectories that will be described later in this paper. Great Lakes data considered here were obtained on Lake Erie during the summer of 1979 at 81°30'W, 42°00'N and on Lake Michigan during the summer of 1977 at 87°00'W and 42°00'N (see large + symbols in Figure 1). Both sites are from 40 to 100 km removed from shoreline aerosol sources. The Lake Michigan site was only 40 to 50 km from, and often downwind of, the Chicago urban complex whereas the Cleveland area was about 70 km from, and less often upwind of, the Lake Erie site.

Comparison of the mass percents (i.e., percentage of total aerosol mass) for each of seven elements observed by Peirson et al. (1974--Britain), King et al. (1976--Cleveland), the 1964-75 U.S. urban mean (Israel, 1974), Stolzenburg and Andren (1981--U.S. rural), and the Lakes Michigan and Erie data sets (after corrections for poor Al recovery) are shown in Table 1. With the occasional deviation of Na the decreasing mass order of the elements is Fe, Al, Pb, Na, Zn, Mn, and Cu for all locations except the Lake Erie data set. In this last case the order is Fe, Zn, Al, Cu, Pb, and Mn, the Zn and Cu relative percents being especially high. Scrutiny of this last column of Table 1 indicates the soil source may have contributed a full order of magnitude less to Lake Erie aerosol mass and chemical character compared with the other locations; the mass percents for Al and Fe (largely soil-derived elements) are tenfold lower in the Lake Erie case. Wet soil conditions and washout by rain showers in the vicinity of and over Lake Erie during and before ship outings is probably the best explanation for the very low soil contribution.

However, the relatively high value of 35 $\mu g\ m^{-3}$ for the total aerosol mass observed over Lake Erie does not readily support the notion that a major source such as soil was so lacking. This dichotomy may be explained by the Lake Erie sulfate (SO_4) mass of 9.6 $\mu g\ m^{-3}$ versus only 5.4 $\mu g\ m^{-3}$ over Lake Michigan; the greater sulfate mass over Lake Erie may have sufficiently offset the low soil source contribution to cause the only 10 $\mu g\ m^{-3}$ total aerosol mass difference over the two lakes.

Can the depleted soil source explain the Lake Erie data set's violation of the compositional uniformity hypothesis? Closer scrutiny of the Great Lakes data is required. Table 2 presents a comparative listing of enrichment factors (EF) for the Lakes Erie and Michigan and UK data sets (including sulfate), and the mass percents and fine/coarse ratios (i.e., ratio of elemental mass concentration in the aerosol of $r < 0.5\ \mu m$ to that in the aerosol of $r > 1\ \mu m$) for Lakes Erie and Michigan. The enrichment factor is a ratio of ratios; the numerator is a ratio of trace elemental concentration to Al concentration for air, and the denominator is the same ratio for soil. Here we use the average soil ratios given by Bowen (1966), but note that all values are considered only approximate. This is not only caused by the poor Al recovery but also by the fact that local Ohio soil dust is probably enriched in Zn, Cu, Mn, and Pb compared to Bowen's bulk soil analysis (Stolzenburg, 1982). The EF Comparison does suggest that, over Lake Erie, Zn and Cu were enhanced, whereas Mn and Pb were depleted. Any contribution by a lake aerosol source could not have caused this result (Sievering et al., 1983). This data set's violation of the compositional uniformity hypothesis does not, then, appear to result wholly from the depleted soil source.

Stolzenburg and Andren (1981) have shown that local industrial sources may cause the contribution of Fe to the aerosol mass to be greater than that of Al and, less often, those for Zn and Mn to be greater than that for Pb. This may have been the cause for [Fe] > [Al] in some cases of Table 1. However, since no industrial sources were within 40 km of the Great Lakes sampling sites, a combination of more distant anthropogenic sources, transport and transformation must have caused Lake Erie EF for Zn and Cu to be so large at the same time that EFs for Mn and Pb are so small.

The Lake Erie data set presents a clear violation of the compositional uniformity hypothesis, despite the fact that the fine/coarse ratios for the elements (except Pb) and also for sulfate are essentially the same over both Lakes Michigan and Erie. Note, however, the more than twofold larger SO_4 mass percent contribution over Lake Erie; the SO_4 mass concentrations of 9.6 $\mu g\ m^{-3}$ over Lake Erie and 5.4 $\mu g\ m^{-3}$ over Lake Michigan constitute 27% and 12% of their respective total aerosol masses. Although no additional chemical analyses were available to characterize the Great Lakes aerosol mass, the substantially greater SO_4 contribution to the aerosol mass over Lake Erie may provide an explanation for the observed violation of the compositional uniformity hypothesis. Further data obtained over Lake Erie provide clues in this regard: 1) aerosol size and number distributions obtained by the ASAS and 2) meteorological back-trajectories.

A simple back-trajectory calculation followed the sampled aerosol from the Lake Erie ship location back toward shore. The back-trajectory procedure druing traverse over water was calculated by a height-weighted average of the ship's horizontal velocity and a triangulation average of reported wind data at 1000 and 2000 ft from the National Weather Service (NWS) upper-level sounding stations at Buffalo, New York, Pittsburgh, Pennsylvania, and Flint, Michigan. When the aerosol reached shore, weighted averages of NWS station data were used to complete the back-trajectory. This overall back-trajectory approach has been compared with seven other trajectory techniques for application to the Lake Erie data base (Jensen, 1981). It was found to be quite accurate even relative to complex computer back-trajectory techniques such as that of Ferber and Heffter (1977).

Figure 1 shows the most likely 24-h, straight-line, back-trajectories. More highly time-resolved trajectories will, of course, follow a different path (but reach the same point after 24 h). The figure shows 21 trajectories; in four cases out of the 25 filter set samples obtained over Lake Erie the meteorological setting was too complex (e.g., lake breeze events) to establish a trajectory. Note that numbers from 1 to 42 appear on Figure 1 next to vertical bars of various lengths. These bars are quantitative indicators of the relative magnitude (and the adjacent numbers qualitative indicators) of the 42 largest SO_2 point sources (USEPA, 1981) in the states of Ohio, Indiana, Illinois, Michigan, and Wisconsin. The 10 largest SO_2 sources on a U.S. state-by-state aggregate basis (Hileman, 1982) are the following (in kilotons yr^{-1}): Ohio (2600), Pennsylvania (2000), Indiana (1950), Illinois (1450), Missouri (1300), Texas (1200), Kentucky (1100), and Florida, West Virginia, and Tennessee (all 1050). Michigan at 900 kilotons yr^{-1}, Wisconsin and the lower peninsular portion of Ontario province, Canada (both at 650 kilotons yr^{-1}) are each substantially smaller SO_2 source areas than Ohio, Pennsylvania, Indiana, or Illinois. It is well known that SO_2 gas is a precursor for SO_4 aerosol. The back-trajectories of Figure 1 show that in all but a few cases (e.g., filter set 1050) there is a very large SO_2 contribution (e.g., filter sets 1090 and 1170) to air parcels later sampled over Lake Erie.

Figure 2 shows a plot of the aerosol number ($\Delta N/\Delta r$) versus size (radius, r) for set 1050 averaged across more than 6-h of ASAS 5-min sampling periods. The sloping solid line is the least-squares best fit to the $\Delta N/\Delta r$ data for $0.13 < r < 1.3$ μm. Figures 3 and 4 are similar plots but for sets 1090 and 1170. The slope of the solid lines are the following: for set 1050, -4.2; for 1090, -5.3; and for 1170, -5.35. Junge (1956) calculated that for an aerosol population to be classified as of natural continental origin the $\Delta N/\Delta r$ slope in this radius range should equal -4.0. Other investigators have since shown that limits of 3.5 to 4.5 are reasonable for classification as a natural continental aerosol population (Israel, 1974). On this basis the aerosol distribution for set 1050 may be claimed to be continental, whereas the distributions for sets 1090 and 1170 are clearly not. Of the 21 filter sets for which ASAS data were obtained, only five had slopes fitting the above continental criterion; they are the five that traversed the state of Michigan (see Figure 1). The mean $\Delta N/\Delta r$ slopes for these five sets (including 1050) is -4.2 ± 0.2; four of these five sets have elemental mass percents that fit the compositional uniformity hypothesis. The mean $\Delta N/\Delta r$ slopes for the remaining 16 filter sets in the ASAS group (including 1090 and 1170) is -5.2 ± 0.4; this is significantly different from that which characterizes a natural continental aerosol population. In all but six of these 16 cases the compositional uniformity hypothesis is clearly violated.

The mean SO_4 concentration for the ten filter sets that do not violate the hypothesis is 3.8 $\mu g\ m^{-3}$; for the remaining 15 sets the mean SO_4 concentration is 11.9 $\mu g\ m^{-3}$. This is especially noteworthy in light of the fact that the SO_4 contribution is largely by small particles as is shown by the fine/coarse ratios in Table 2. Further, the example comparison of Figures 3 and 4 with Figure 2 shows that below 0.2 μm radius the aerosol population is a full order of magnitude greater for those sets that violate the hypothesis (sets 1090 and 1170) than for the set that does not (set 1050). These data suggest that the SO_4 conversion process may be an important contributor to the compositional nonuniformity observed in the case of the Lake Erie data set. Certainly simple dilution can not account for the observed elemental concentration differences, since the continental slope criterion would then be observed. In any event, there is a clear enhancement of $<$ 0.2 μm radius aerosol for those cases when the chemical uniformity hypothesis is violated. This in turn suggests that more distant anthropogenic source aerosol may cause nonuniformity in chemical composition just as local sources are known to cause this nonuniformity. Thus, it does not appear that chemical uniformity of continental atmospheric aerosol removed $\sim$ 100 km from anthropogenic sources is necessarily to be expected. Until further evidence is found identifying and explaining exceptions to the "rule" as well as supporting generality of the chemical uniformity hypothesis, it should remain a hypothesis only.

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TABLE 1. Percentage of Total Aerosol Mass for Each of Seven Elements

Element	Great Britain	Cleveland		U.S. Urban	U.S. Rural	Lake Michigan	Lake Erie
		Urban	Suburban				
Fe	0.9	3.8	3.8	1.5	1.8	1.1	0.13
Al	0.6	2.5	4.0	*	2.0	~1.0	~0.1
Pb	0.35	0.65	1.1	0.75	0.5	0.5	0.01
Na	2.5	0.7	0.8	*	0.4	*	*
Zn	0.35	0.35	0.55	0.65	0.1	0.2	0.11
Mn	0.05	0.1	0.15	0.10	0.06	0.05	0.002
Cu	0.04	0.1	0.15	0.09	0.05	0.04	0.03
Aerosol Mass ($\mu g\ m^{-3}$)	~45	115	45	105	40	45	35

* no data available

TABLE 2. Aerosol statistics for Lakes Erie and Michigan, and comparisons of their enrichment factors with those observed by Peirson *et al.* over Great Britian

Element	Dry Mass Percent		Fine/Coarse Ratio		Enrichment Factors		
	Erie	Michigan	Erie	Michigan	Erie	Michigan	UK
Al	∼0.1	0.6	1.8	1.2	1	1	1
Fe	0.13	1.1	1.9	1.6	∼2.4	∼2.1	∼2.9
Pb	0.01	0.5	5.9	13	∼720	∼3200	3700
Zn	0.11	0.2	4.8	6.1	∼1500	∼320	925
Mn	0.002	0.05	2.1	2.0	∼2.0	∼5.9	9.9
Cu	0.03	0.04	3.3	3.9	∼1100	∼120	165
SO_4	27	12	23	27	n.a.	n.a.	n.a.

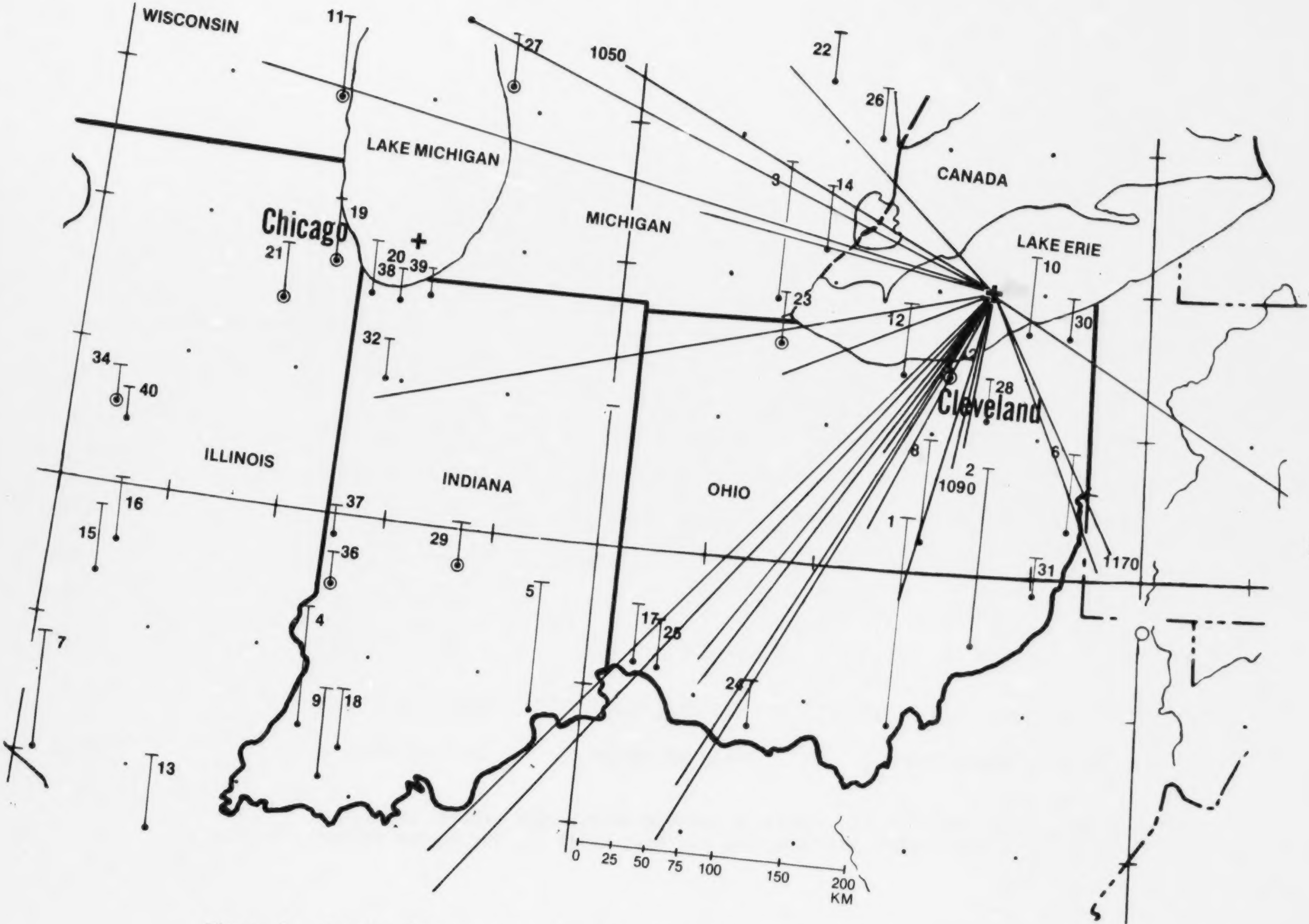
WISCONSIN
LAKE MICHIGAN
Chicago
MICHIGAN
CANADA
LAKE ERIE
Cleveland
ILLINOIS
INDIANA
OHIO
1050
1090
1170
11
27
22
26
3
14
19
21
20
38
39
23
12
10
30
28
32
34
40
8
2
6
16
15
37
36
29
1
31
5
17
25
4
7
9
18
24
13
0
25
50
75
100
150
200
KM

Figure 1. Great Lakes study region with the most likely 24-h, straight-line back-trajectories for each of 21 filter set samples. The 42 largest SO_4 point sources in this region are also shown.

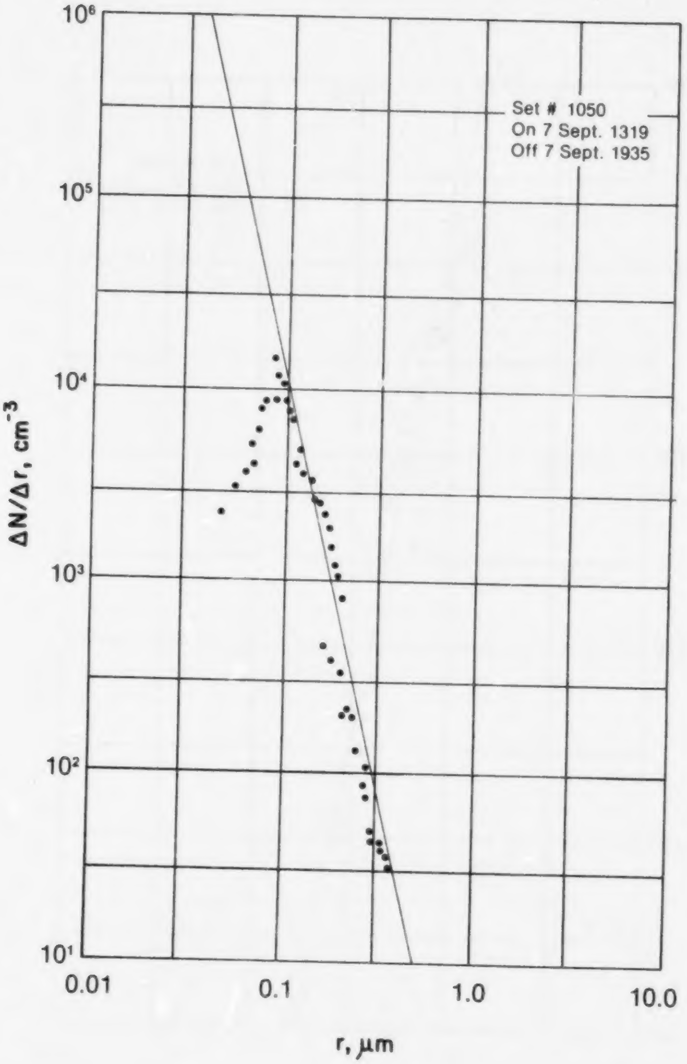

Figure 2. Aerosol number versus aerosol radius for filter set #1050.

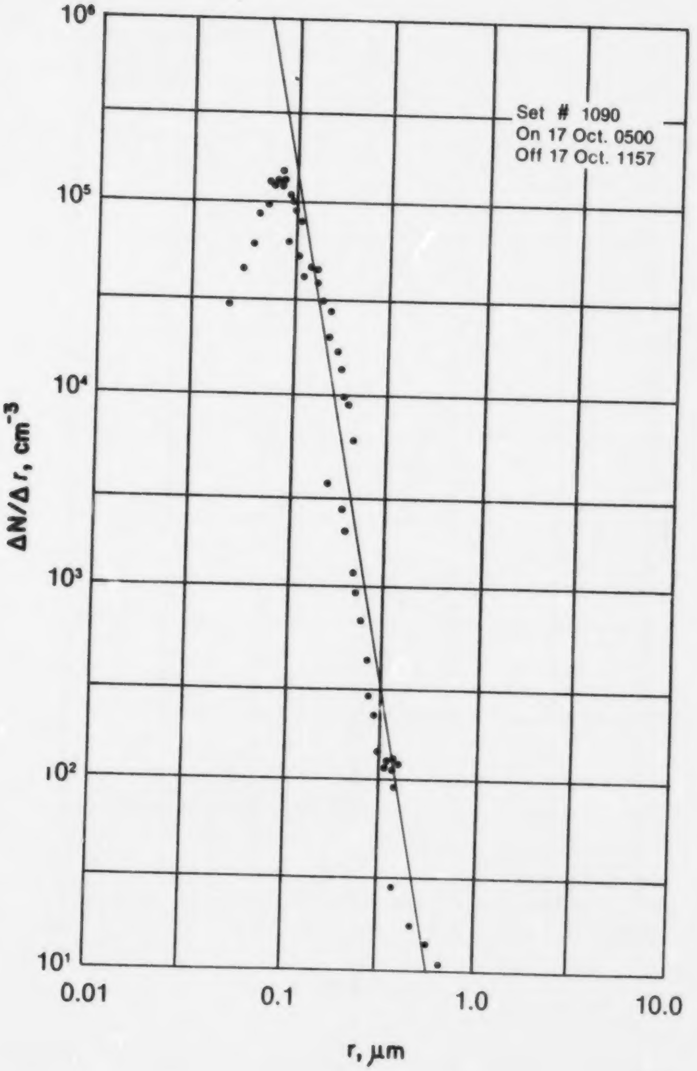

Figure 3. Aeorsol number versus aerosol radius for filter set #1090.

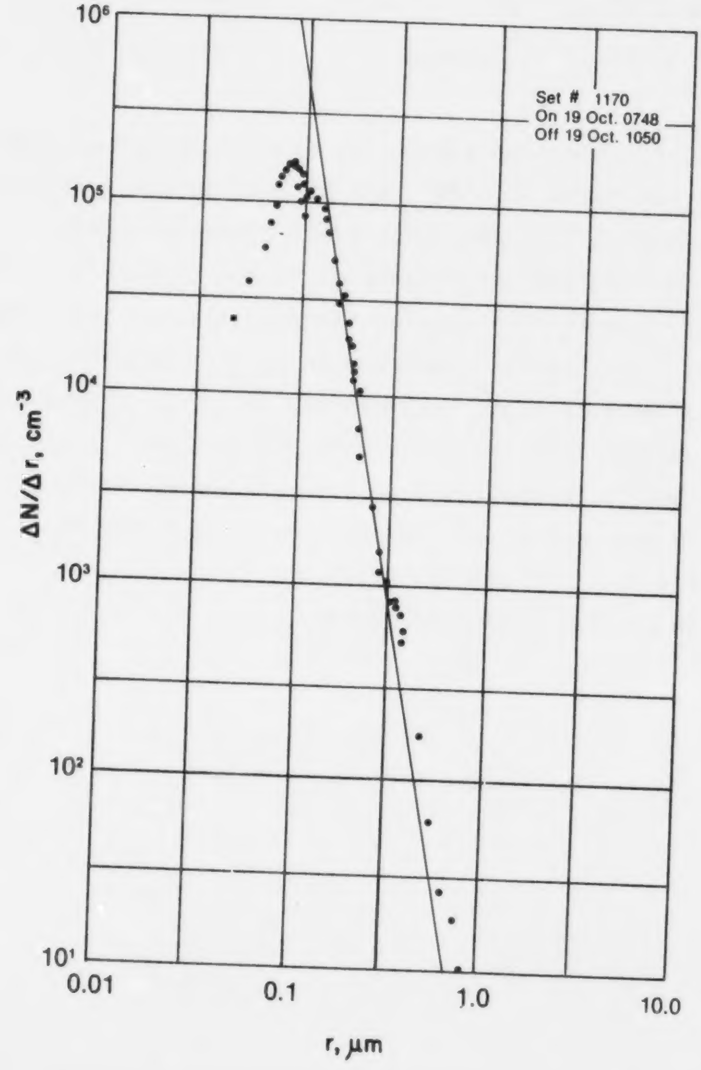

Figure 4. Aerosol number versus aerosol radius for filter set #1170.

APPENDIX C

TECHNICAL NOTE

TRACE ELEMENT PASS-THROUGH FOR CELLULOSE IMPACTOR SUBSTRATES AND FILTERS WHEN USED FOR AEROSOL COLLECTION

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ABSTRACT

Filter papers and impaction substrates made of cellulose fibers, such as Whatman 41 and Misco P810/252, are of considerable utility in the collection of aerosol for subsequent trace elemental analysis. This experiment evaluated the performance of Misco P810/252 in collecting trace elements, relative to a co-located standard glass fiber filter hi-vol collection. Sampling was conducted in varying meteorological conditions, so that results might be expressed in terms of environmental variables such as temperature and relative humidity. The pass-through factors presented here were derived from a series of environmental samples collected over land and over water. Overall mean cellulose Misco filter collection of Pb and Zn was found to be 38% and 32% less than that collected on the glass fiber filter.

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EXPERIMENTAL DESIGN AND EXECUTION

The purpose of the experiment was to compare the collection efficiency of the Misco cellulose impactor substrates and filter in a modified Sierra 1-, 3-, 6-slot impactor with the assumed near-100-percent collection efficiency standard type A glass fiber filter. The problem, restated, is to determine if the total concentration computed from the sum of impactor stages 1 and 3, and backup filter, stage 6, can be related to the total concentration of aerosol gravimetrically measured with standard type A glass fiber filters. This experiment, then, has particular significance for data of Sievering et al. (1980) and Duce et al. (1976), since all trace element and nutrient data for aerosol over Lakes Michigan and Erie were collected using the Misco cellulose media.

All aerosol collection was done with paired flow-controlled hi-vol ($1.1 \ m^3 \ min^{-1}$) samplers. Flow rates of the samplers were recalibrated after each group of five sampling runs, approximately one- to two-week intervals, to assure comparability of sample volumes. The samplers were set up not less than three meters apart, and were fitted with plastic exhaust hoses to minimize reentrainment of copper aerosol shed by pump commutators. One pair of samplers was operated at the Governors State University air quality monitoring site from March to August, 1980. A second sampler pair collected aerosol at the city of Chicago 68th Street crib from June to August, 1980. A filter holder cassette containing, in order, Misco slotted substrates on stages 1 and 3 and a 20 by 25 centimeter Misco filter on one hi-vol sampler; a standard type A glass fiber 20 by 25 centimeter mat was used on the other sampler. Behind each of these filter cassettes, separated by 0.5 centimeters and supported by fine stainless steel screen, was mounted a "second backup," a type A glass fiber mat, of Gelman Spectrograde material. The Spectrograde filters collect aerosol as the standard type A, but have a lower trace element blank. In all, then, there were six parts to each concurrently collected set of filters: the three-stage Misco impactor/backup with its spectrograde second backup, and the type A filter with its Spectrograde backup. These parts were designated M1, M3, M6, SGM, and A, SGA, respectively. Sets of filters were exposed for periods ranging from 24 to 96 hours, depending on variability of meteorological conditions over the sampling period and degree of pollution loading prevailing. In general, an effort was made to conduct sampling on a given set during similar conditions, so that parameters derived for that sample could be related to meteorological variables. Each fifth sample was a field blank, in which the filters were carried through the entire procedure, except that the hi-vol motors remained off during the exposure period, usually 24 hours for the field blanks. Several unexposed blanks were also used, where the filters were carried through all of the procedure except mounting on the hi-vols. In all, 37 samples and 16 blanks were collected during the course of the experiment.

Continuous monitoring of ambient temperature, wind speed, wind direction, barometric pressure, and relative humidity was done at Governors State throughout the experiment. In addition, wind speed, wind direction, temperature, and relative humidity were recorded hourly at the 68th Street Crib while sampling was being conducted there. These data were averaged for each period during which a set of filters was being exposed. The mean values were then used to characterize each period. At the Governors State site, two optical particle-counting devices continuously monitored particulate levels. Results from an automatic condensation nuclei counter (Environment One Corp. Rich 100) and an integrating nephelometer (Meteorology Research Inc. Model 1550) were similarly averaged over each sampling period.

Analysis of the various filter stages followed several different procedures. The M1, M3, and M6 stages were first trimmed with Teflon-coated stainless steel scissors to remove the unexposed edges. The exposed portions were then placed in fused quartz combustion boats which had been acid washed with Ultrex HCl. The boats were then run in a low temperature oxygen plasma asher (Plasmod Inc.) at 75 watts PF for about 24 hours, i.e., until all the cellulose filter material was oxidized. The residue was then brought into solution with hot 12N Ultrex HCl, and volume-normalized with distilled deionized water. The SGA and SGM stages were gravimetrically analyzed for total aerosol mass, and then were trimmed of unexposed parts, cut into strips, and leached in a boiling HCl + HNO_3 bath for 60 minutes. These filters were then rinsed with distilled deionized water and the leachate brought to a normalizing volume. The type A filters were gravimetrically analyzed for total aerosol mass only. The liquid samples resulting from the preparation of the M1, M3, M6, SGA, and SGM filters were then analyzed by atomic absorption spectrophotometry for Pb, Zn, and Fe.

RESULTS

As can be seen in Table 1, the overall mean concentrations of Pb, Zn, and Fe fall within the range of concentrations for these elements in aerosol in the Great Lakes region and elsewhere. Samples in this study were collected on a routine 24- to 96-h run-time basis, while the overlake samples' run-times were much shorter, usually 3- to 6-h. The longer run-times for the pass-through experiment were necessary in order to collect sufficient material on the second stage backup filters, SGA and SGM. Even with the extended run-times, Fe on these stages was quite often below analytical detection limits. (NOTE: detection limits, laboratory and field blanks for the pass-through samples were comparable to the values reported for Lake Michigan sampling [Sievering et al., 1980]).

Still, the pass-through factors (PTF) reported here,

$$PTF = \frac{C_{SGM} - C_{SGA}}{C_{M1,3,6} + C_{SGM}} \bullet 100\%$$

should be representative of the percentage amounts of material missed by the three-stage modified Sierra 1, 3, 6 slot impactor and Misco cellulose media, as used in several studies. The PTF values given here would most likely be slight underestimates, as loading of the filter below a critical stage should only slightly increase its collection efficiency.

The value of PTF for Pb and Zn not only can be applied to those elements, but also to other fine particle ($D < 1.0$ μm) associated elements. Similarly, the PTF for Fe reported here could also apply to similarly particle-size associated elements ($D > 1.0$ μm). Table 1 gives the overall mean PTF for each of the three elements measured. Table 2 shows some of the stronger associations that could be found between the measured parameters. Although the correlation coefficients are very weak, expected general trends appear. PTF and percent concentration fine aerosol (%F) seem to be directly related. RH is weakly and inversely related with PTF, as would be expected due to the hygroscopic nature of the cellulosic media. Percent fine aerosol association is defined here as:

$$\%F = \frac{C_{M6}}{C_{M1,3,6}} \cdot 100\%$$

Separation of the five highest and lowest RH cases and computation of PTF values for those regimes, shown in Table 1, again reflects the inverse relationship, but without strong statistical significance. (NOTE: Fe was undetectable in most of these ten cases.)

The main conclusion of this study, then, is that the overall mean PTF values in Table 1 are relevant correction factors for the size-fractionate trace element in aerosol data of Sievering et al. (1980), and Duce et al. (1976) and others. Based on %F as a convenient, although low-resolution, size-association indicator, the PTF results for Pb, Zn, and Fe can probably be reasonably extended to other elements in the overlake detabase. Applicability of these PTF values to fine aerosol data collected via cellulosic media by other researchers would require a careful evaluation of the exact sampling technique employed, but will hopefully be useful.

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Table 1. Mean Pass-Through Factors (PTF) and Concentrations (C).

	C, ng m^{-3}			PTF, percent		
	Pb	Zn	Fe	Pb	Zn	Fe
Overall	109	61	165	37.6 ± 6.4	31.9 ± 6.1	11.9 ± 3.3
RH > 88	202	84	nd	36.1 ± 12.1	30.7 ± 10.3	nd
RH < 65	80	47	nd	42.8 ± 10.8	38.2 ± 12.6	nd

Table 2. Some Correlations Between Variables.

	PTF (Zn)	%F (Pb)	%F (Zn)	RH
PTF (Pb)	+.52	+.25	+.44	-.24
PTF (Zn)		+.23	+.84	-.19
%F (Pb)			-.19	+.15
%F (Zn)				+.11

F = Fine aerosol ($D < 1$ μm)

APPENDIX D

CHEMICAL ELEMENTS IN ATMOSPHERIC AEROSOL OVER SOUTHERN LAKE MICHIGAN:
THE CONTRIBUTION OF THE LAKE SOURCE

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ABSTRACT

Chemical element balance analysis was applied to atmospheric aerosol data obtained over Lake Michigan for 12 elements, in order to ascertain the contribution of each of seven source types, especially Lake Michigan itself. It was found that the lake contributed about twice as much to total aerosol mass in both diameter $d < 1 \mu m$ (fine) and $d > 1 \mu m$ (coarse) aerosols as did soil, although the soil source aerosol contribution may have been anomalously low. The fine aerosol lake source appears to be dependent upon mean windspeed; the coarse aerosol lake source appears to function most of the time.

The samples were collected from May 1978 through January 1979, on cellulose media with modified Sierra cascade impactors. Summer and fall sampling predominated. Sampling was done at a City of Chicago water intake crib, 3.2 km from shore on southern Lake Michigan, $87^{o}32'W$, $41^{o}47'N$. Air concentrations were determined by inductively coupled Ar plasma atomic emission spectroscopy. Mean concentrations were generally 2 to 4 times higher than means observed one year earlier at midlake, $87^{o}00'W$, $42^{o}00'N$, 50 km from the nearshore crib site. Size distributions of the elements were similar at both sites, except for those of Ca and Mg which appear to be due to the lake source.

INTRODUCTION

The urban-industrial complex surrounding the southwestern and southern shore of Lake Michigan contributes significant amounts of anthropogenic aerosol to the atmosphere. Prevailing winds in this region give rise to particle trajectories that pass over the lake more than 70 percent of the year (NOAA, 1975). Mesoscale recirculation by lake breeze events (Lyons and Olsson, 1973), unstable spring and autumnal air overlake, and enhanced turbulence during non-steady-state conditions (Hughes and Sievering, 1982) increase the probability of atmospheric pollutant aerosol contributing to the chemical loading of Lake Michigan. The extent and intensity of the Chicago regional air pollution source (Winchester and Nifong, 1971; Gatz, 1975) is such that moderately efficient ($\sim$10 percent) transfer between air and water would be detrimental to water quality in the lake. Trace metals (Eisenreich, Emmling, and Beeton, 1977; Dolske and Sievering, 1979) and nutrients (Murphy and Doskey, 1977; Dolske and Sievering, 1980) have been increasingly implicated as significant atmospheric contributions to the total pollutant burden of Lake Michigan.

Processes affecting the overlake transport and deposition of pollutant aerosol are complex and not well understood. In order to expand the chemical and physical characterization of aerosols over southern Lake Michigan, much research has been conducted in recent years. Sievering et al. (1979) collected aerosol and meteorological data in 1977 at a midlake site (87^o00'W, 42^o00'N). Data, reported here, were collected at the City of Chicago 68th Street water intake crib (87^o32'W, 41^{o}47'N) from May 1978 through January 1979. Several recent aerosol sampling programs (Williams and Muhlbaier, 1978; Fingleton and Robbins, 1980) also collected data at the crib site. Comparison of these crib data with the 1977 midlake data is here undertaken to lend insight regarding the overlake transport and chemical character of particulate matter. Further, chemical element balance (Gordon, 1980; Cooper and Watson, 1980) analysis was undertaken to quantify the contribution of several aerosol source types to the particulate matter observed at the crib site.

METHODS

In May and June 1978, flow-controlled high-volume samplers (General Metal works, GMW 2000) were operated at the upper box-beam bridge which runs between the two main buildings of the crib (see figure 1). The sampler intakes were 13 m above the lake surface, midway between the two structures. Standard meteorological sensors were also located at the position. A digital system recorded and printed 15-min means for the continuously-monitored meteorological parameters. From July 1978 to January 1979, the hi-vol samplers were operated on the lower bridge of the crib 6 m above the surface. During these months, the meteorological sensors were placed on a movable, 3-m mast which was erected on the upwind side of the hexagonal sea wall for each day's sampling.

In order to eliminate contamination from daily operation at the crib, permissible wind direction (WD) sectors were defined. Samples were considered valid only if WD ± 1σ for the entire sampling period was within the sectors $40^0 < WD < 130^0$ or $210^0 < WD < 330^0$ (see figure 1). The samples were collected on cellulose impactor substrates (MISCO P252A) and 20 x 25 cm backup filters (MISCO P810A). Sierra #235 five-stage impactors--modified to use only stages #1 and #3 along with the backup--were exposed at 1.13 m^3 min^{-1} (40 SCFM) for periods of 3 to 7 hours. This length of exposure was sufficient to collect enough aerosol for the chemical analyses, yet short enough for meteorological parameters to remain fairly constant during each sampling period.

The exposed cellulose filters were analyzed by two separate methods. The impactor strips and about one-half of the backup filter were oxygen-plasma ashed at 75 watts RF. The ash residue was dissolved in hot 6 N HNO_3 and brought to a standard volume with distilled deionized water. This procedure gave three subsamples for each filter set: two impactor stages (#1 and #3) collect coarse particles of diameter (d) > 1.0 μm while the backup collects fine particles, d <1μm. All three subsamples were analyzed by inductively coupled Ar plasma atomic emission spectroscopy (ICAP). Elements identified were Al, Ca, Cd, Cu, Fe, Mg, Mn, Mo, Na, Ni, Pb, Ti, Sn, V, and Zn. Samples taken concurrently and prepared by an alternate method (Dolske and Sievering, 1980) were analyzed at USEPA-Central Regional Laboratory for total phosphorus, nitrate, and sulfate by automated colorimetric methods. A summary of trace metal analytic detection limits, procedural blanks, and typical sample values is given in Table I. Note that Al values may be somewhat low since HF dissolution was not used. It should also be noted that ICAP Cu data are considered valid not only because the procedural blank value is small when compared with typical samples, but also because the hi-vol motor exhaust was separated from the filter sampling.

Duplicate analyses of replicate samples and samples into which known amounts of certain elements were spiked (Cu, Pb, Zn) indicate that ICAP results were reproducible to within ± 20 percent. A second portion of the backup filter from 12 filter sets was sent to Argonne National Laboratory for x-ray fluorescence (XRF) analysis of Br, Fe, Mn, Ni, Pb, Se, and Zn content. The results of this limited analytical intercomparison are given in Table II. For Pb, Zn, and Fe the concentrations were in fairly good agreement, but the XRF results for Mn and Ni gave consistently higher concentrations, resulting in large percent differences from ICAP concentrations. The concentration values in the second column of Table II are means of all analytical results from both ICAP and XRF. Br and Se were not included in the ICAP analyses.

Meteorological data collected at the crib were complemented by hourly reports from National Weather Service and U.S. Coast Guard stations around southern Lake Michigan. Also, during the May 1978 sampling period, a National Center for Atmospheric Research aircraft collected meteorological and aerosol number concentration data during flights that included the crib site as a sampling point (Hughes and Sievering, 1982). From these data, a simplified back-trajectory calculation determined the horizontal and vertical spread of the aerosol collected at the crib. The horizontal spread in the trajectory was assumed to lie within two standard deviations about the mean wind direction. The vertical spread was determined through the application of stability category dispersion coefficients determined as a function of the bulk Richardson number (Nagib, 1978).

RESULTS

The back-trajectory data sets are divided into two distinct groups. The first consists of data representing a direct Chicago-area-to-crib traverse (figure 2a, for example). The second group consists of data representing aerosol trajectories strongly influenced by a lake breeze recirculation (figure 2b). The source area for all the data sets appears to have been the general Chicago region (including Gary, Indiana), regardless of the wind direction prevailing at the crib during aerosol collection. This was the result of restrictions placed on mean WD for the entire set for valid, uncontaminated samples, and the small vertical rise in trajectories upon reaching shore.

Rahn (1976) has concluded that geometric means may be the most appropriate representation of environmental concentrations of trace elements for they tend to have lognormal distributions. A direct comparison of nearshore and midlake geometric mean concentrations of 16 elements and compounds is shown in Table III. The concentrations are geometric means for all data sets collected where the wind direction was within permissible sectors; each data set's concentration is the arithmetic sum of analytical results for the impactor stages and the backup filter. For aerosol collected at the midlake site (87°00'W, 42°00'N), sampling, analytical, and trajectory-plotting methods used in 1977 (Sievering et al., 1979) were the same as those used at the crib in 1978, so the two data sets should be comparable.

In general, mean concentrations at the crib site were two to four times greater than the midlake means (Table III). A few elements (Cd, Mo, Ni, V) that were below ICAP detection limit at midlake appeared in the nearshore samples. This was not an unexpected result because of the proximity of the crib site to the intense Chicago regional aerosol source. The mean concentrations at the midlake point were, in turn, five to more than thirty times higher than the continental background concentrations given by Rahn (1976).

It is interesting to note, however, that while the concentration of nearly all elements were much higher at the nearshore site, aerosol elemental composition was essentially unchanged. Enrichment factors for each element of interest, x, were calculated using the average composition of soils given by Bowen (1966):

$$EF = \frac{\bar{C}\ (x)}{C\ (\text{indicator})}\ (\text{aerosol}) \Bigg/ \frac{\bar{C}\ (x)}{C\ (\text{indicator})}\ (\text{soil})$$

Al was used as the soil-derived or natural-background aerosol indicator element, with EF = 1. Values of EF > 1 indicate that an element is present in amounts greater than might be expected from the natural, soil-derived source. From Table IV, it can be seen that the most highly enriched elements are Cd, Pb, Zn, Mo, Ni, and Cu.

The impactor arrangement used allows the first impactor stage to be taken as collecting only coarse ($d > 1\ \mu m$) particles. The second impactor stage improves resolution between the coarse mode (1st stage) and fine mode (backup). The distribution of an element with respect to particle size can be crudely shown by a ratio between the fine and coarse particle concentrations of that element:

$$\text{Fine/Coarse Fraction} = \frac{C\ (\text{backup})}{C\ (\text{1st stage})}$$

In Table IV, the fine/coarse fractions for the crib samples and midlake samples are compared. For most elements there are no significant differences between the two data sets. A fraction greater than one indicates that the element is concentrated in the $d < 1$ μm or fine particle range. Note that this is the case for all of the high-EF, anthropogenic elements.

Another descriptor of the elemental content of the aerosol is percent mass composition:

$$\% \text{ mass composition} = \frac{\bar{C}\,(x)}{\bar{C}\,(\text{total aerosol})} ,$$

where $\bar{C}$ (total aerosol) has been gravimetrically determined from standard type-A glass fiber filters (20 x 25 cm). The values calculated here (Table IV) conform closely to the data of Gatz (1975) for Chicago aerosol and to the midlake values that had trajectories indicating the presence of the Chicago source aerosol.

DISCUSSION

Comparing the 1978 crib-site concentrations with the 1977 midlake-site concentrations leads to two observations regarding qualitative effects of overlake transport on the Chicago region source aerosol. (Caution is expressed regarding quantitative comparison of the two data sets since a number of factors may contribute to their differences.) First, the fine/coarse fractions and % mass compositions (Table IV) reveal three groups of elements. For Pb, Zn, and S the fine/coarse fractions are slightly greater at midlake than at the crib while their % mass compositions are less. (Of the elements identified by ICAP, these are more strongly associated with fine particles.) Sedimentation loss of coarse particles, gas-to-particle reactions, and coagulative growth could all contribute to this outcome. For Al, Cu, Fe, and Mn (and possibly N and P) the fine/coarse fraction was slightly larger nearshore. In contrast to these two groups, Ca and Mg show large, significant differences between fine/coarse fractions at midlake and nearshore (a factor of three or more). The decrease in Ca and Mg fine/coarse fractions during overlake transport might be due to the generation of aerosol by the lake itself.

A second qualitative observation concerns the effect of lake-breeze-induced mesoscale recirculation on the nature of crib-site aerosol. Of the 23 crib filter sets, 18 could be separated into two groups; those with which no lake breeze event was associated, and those for which a well-developed mesoscale recirculation was indicated by surface and aircraft data. For the lake breeze case data, overall concentrations at the crib site were slightly lower than at midlake. This point is consistent with large-particle sedimentation loss and dilution, as well as aerosol aging within the recirculating plume (Lyons and Olsson, 1973). EFs for the two groupings of 8 lake-breeze and 10 no-lake-breeze filter sets show no substantial differences except for Ca and Mg. For these two elements, EFs are two and one-half times larger for the no-lake-breeze group than for the lake-breeze group. This appears, at first, peculiar since aerosol in a lake-breeze trajectory are present over the lake far longer than are those aerosol in a nearly direct trajectory from shore to the crib site. However, the mean windspeed at the crib was 3.4 ± 1.5 ms^{-1} for the 8 lake-breeze filter sets and 6.0 ± 1.0 ms^{-1} for the 10 no-lake-breeze filter sets. The combination of light winds (< 5 ms^{-1}) and thermally stable air present over the lake during lake-breeze events could "shut off" the lake aerosol source whereas winds greater than 5 ms^{-1} might introduce a lake source component to the total aerosol observed at the crib site.

Chemical Element Balance (CEB)

Since both qualitative observations above suggest a lake source contribution to aerosol chemical character over Lake Michigan, a source reconciliation was attempted using the chemical element balance (CEB) approach (Gordon, 1980; Cooper and Watson, 1980). The computer analysis developed by Watson (1979) was used, affording both fine and coarse fraction aerosol source reconciliation. This particular computer analysis is especially useful when considering the crib site data since the uncertainty in each calculated source contribution is also determined. The reason this latter point is useful is that the identification of a lake aerosol source may be confused by the cement limestone manufacturing (or, less likely, a soil-like anthropogenic) aerosol source; or highway or road dust which are all similar to the lake source and also prevalent in the Chicago region (Gatz, 1975; Winchester and Nifong, 1971). This problem may be ameliorated somewhat by adding Na filter sets' data since Lake Michigan dissolved and suspended solids are about 2% Na by weight (Torrey, 1976) whereas the cement manufacturing source aerosols are known to be less than 0.001% Na by weight (Kowalcyzk and Gordon, 1979). Because of high blank levels, Na concentrations could not be determined for 5 of 23 filter sets' data aggregated to give Tables III and IV results. The remaining 18 may, however, be considered in discriminating between the lake and cement manufacturing sources. Seventeen of these 18 sets were obtained before December so that the road-salting Na source may be discounted. Of course, Na in soil, fuel oil, and coal must also be considered. Then there is the ubiquitous sea salt source. The purpose of the CEB approach is to account for these multiple source contributions for each of the elements monitored.

Seven source types were here considered: the lake source (hereafter, LAKE); a soil source (SOIL); a cement manufacturing source (CEMENT); an iron and steel manufacturing source (STEEL); a coal burning source (COAL); a fuel oil burning source (OIL); and an automobile source (AUTO). Table V lists the elemental composition--including uncertainties--for each of these seven source types. Notice that Ti was included. (For all 18 filter sets being considered, Ti concentrations were significantly above their procedural blank values.) Since Ti may help in distinguishing between SOIL and COAL it was included in the CEB analysis. Ni, Mo, and Sn were not included since there were too many instances for which their fine or coarse mode concentrations were not sufficiently above procedural blanks. (These three elements contribute < 0.01% [or an unknown amount] to all seven of the aerosol sources in Table V.)

The seven source types were chosen on the basis that they probably contribute the large majority of mass for the 12 elements in Table V. except Na and possibly Zn (Gatz, 1975). The elemental composition of each source (its "fingerprint") was determined by combining Chicago-region data with published statements of relative mass contribution--primarily those of Gatz, 1975; Kowalcyzk and Gordon, 1979; Ondov et al., 1979.

Detailed information on dolomite limestone used to make cement (Lamar and Thomas, 1956) shows that Chicago-region limestone quarries contain, on average, only about two and one-half times more Ca than Mg, whereas, finished cement contains 35 to 40 times more Ca than Mg. The emission source for cement manufacturing is almost entirely caused by mining in the quarries; thus, the use of Lamar and Thomas' quarry analyses instead of finished cement analyses to specify the CEMENT elemental source composition. Notice the large uncertainty in weight percent for both CEMENT Ca and Mg. This is due to the wide variation in their content from quarry to quarry. LAKE was determined using Torrey's (1976) review of Lake Michigan chemical data. Total dissolved solid and total suspended particulate contributions were summed to arrive at each element's LAKE contribution. LAKE assumes no enrichment of elements during aerosol emission at air/water interface.

A comparison of LAKE and CEMENT shows that the ratio of Ca to Mg as well as the weight percent for Fe and Na may afford the separation of LAKE contributions from those of CEMENT. No previous literature source composition for LAKE is available for this comparison, but most literature cement manufacturing compositions (Gatz, 1975; Winchester and Nifong, 1971) assumed emissions "to have the same composition as the finished product" and, thus, an inappropriate low weight percent of Mg. There is also about 65% and about 75% more Fe and Al, respectively, in CEMENT than was indicated by Gatz (1975). The Mn content is about the same as was assumed by Kowalczk and Gordon (1979) although, as in the case of Mg, the Mn content in quarries is quite variable or unknown. CEMENT, as specified in Table V, actually causes more difficulty in distinguishing it from LAKE than if literature cement source compositions had been used.

Distinguishing SOIL from COAL has also been shown to be quite difficult. In fact, Cooper and Watson (1980) point out that soil, road dust, rock crusher, asphalt production and coal source contributions "cannot readily be distinguished on the basis of their elemental fingerprints and are usually grouped into a common source category." This is especially true in the present context since the elemental concentrations of Br, K and S were not determined. In setting out to distinguish SOIL and COAL it was felt that COAL would be a major contributor to the fine fraction aerosol but not to the coarse fraction (Ondov et al., 1979) whereas road dust, rock crusher and asphalt production sources would fractionate about the same as SOIL by aerosol size. SOIL may therefore be seen as representing some anthropogenic soil-like aerosol sources as well as the natural soil source itself.

The midwestern soil composition of Bowen (1966) provided the elemental fingerprint for SOIL in Table V. This is essentially the same soil "fingerprint" used by Gatz (1975) in previous Chicago-region CEB interpretive analysis. The coal source composition was specified using Ondov et al. (1979) as the primary data source. Commonwealth Edison (1981) was contacted to confirm that cold-side electrostatic precipitators are used (almost exclusively) as pollution control devices on their coal-fired power plants and that western coal is by far the primary coal type burned. Thus, the data of Ondov et al. (1979) is especially appropriate. However, it was found (Commonwealth Edison, 1981) that the concentration of Cd and Zn are approximately 30 times and 3 times higher, respectively, and V approximately 3 times lower in the strains of locally burned coal than in that considered by Ondov et al. (1979). COAL in Table V directly reflects this in its distinction from the Ondov et al. (1979) coal "fingerprint." A comparison of COAL (Table V) with a previously identified Chicago-region coal source (Gatz, 1975) shows some differences. The ratio of Gatz's values to COAL are (in parens): Al (1.0), Ca (1.3), Cd (2.5), Fe (2.1), Mg (0.7), Mn (0.6), Pb (12), V (2.7), Zn (2.2), Na (0.2) and Ti (1.1). These differences are primarily the result of a more careful consideration in COAL of the coal type and pollution control devices used by coal-fired power plants in the Chicago-region.

Notice again, though, the large uncertainties specified, especially for Cd, Pb and V, due to ill-knowledge of certain elemental weight contributions.

STEEL in Table V has nearly the same source composition as was earlier specified by Gatz (1975) and Winchester and Nifong (1971) except that recent emission measurements from a number of steel manufacturing plants (Lake-Porter Air Pollution Task Force, 1981) showed one-third lower concentrations of Ca, and very slightly lower Cu, Fe and Mg concentrations.

OIL in Table V is almost identical to the oil source composition of Kowalcyzk and Gordon (1979) since actual oil-burning emissions were analyzed for Al, Ca, Cu, Fe, Pb and Zn as well as V and Na. Finally, AUTO is also nearly the same as the auto source composition of Kowalcyzk and Gordon (1979) except that the weight percent of Pb was reduced from 40% to 25% given the changing mix of leaded/unleaded automobile fuel use (Illinois Chamber of Commerce, 1981).

The Table V source types and the 18 crib filter sets for which all 12 elemental mass concentrations are available were used to perform CEB analysis on a set-by-set basis for both the fine fraction and coarse fraction elemental masses. It was first confirmed that each element's mass concentration could be fully explained by a six-source linear combination (excluding either CEMENT or LAKE), except Na and Zn concentrations. The Table VI results show the mean ratio of CEB calculated to observed concentrations for Ca, Fe, Mg, Mn, as well as for Na and Zn. The mean percent Na explained (across the 18 sets considered) is 40% for the fine fraction mass and 88% in the coarse fraction mass when LAKE is considered in linear combination with the last five sources of Table V. Invoking a sea salt mass concentration, in no case greater than 0.25 $\mu g\ m^{-3}$, completely explains the residual Na mass with the concomitant introduction, by the sea source, of no more than a 3% enhancement of Ca and Mg. The explained Zn may be low due to neglect of an incineration source because it could not be well specified. There is also some possibility that one of the anthropogenic soil-like aerosol sources (such as road dust) which is enriched in Zn may explain some of the residual Zn. However, it will be seen below that SOIL, representing these anthropogenic soil-like aerosol sources (partly) as well as the natural soil source, was a relatively small contributor to the total aerosol mass. The otherwise exceptional fit of the six-source linear combination (using either LAKE or CEMENT) to the elemental mass data base for both fine and coarse fractions warrants the presentation of the overall CEB results.

CEB Source Reconciliation

The mean ratio of calculated CEB to actual observed elemental concentrations was very nearly 1.0 when taking a six-source combination, using either LAKE or CEMENT separately, as Table VI shows. However, uncertainty in these Table VI ratios were substantially greater when CEMENT was used as opposed to LAKE. In the case of Mn, an overall uncertainty of 20% results from use of LAKE versus 37% from use of CEMENT; for Fe these uncertainties are 14% and 29%, respectively. Uncertainty for Mg was 18% and 110% respectively for LAKE and CEMENT. Clearly, LAKE better explains the set-by-set crib-site data than does CEMENT, when one or the other is used in combination with the remaining five sources of Table V.

We are also interested in the relative contributions of the seven sources to the overall elemental concentrations at the crib site. A linear combination of all seven sources was used to obtain the CEB results in Table VII for both FINE (fine fraction) and COARSE (coarse fraction) mass loadings--relative to a soil source of unit (1.0) magnitude. Since too few filter sets had an associated total aerosol mass, the results must be presented as relative magnitudes; that is, CEB analysis was performed instead of chemical mass balance (CMB) analysis. The range in relative source contributions is quite large (except for COAL). Therefore, only approximate mean ratios are stated in Table VII, again excepting COAL. The Table V source contributions of COAL and SOIL are quite similar, so the mean ratio of FINE COAL to SOIL is a rather constant 0.55 ± 0.06. As an example of confidence in Table V source contributions the mean uncertainties for FINE SOIL and FINE COAL are 32% and 34%, respectively. These small uncertainties justify strong confidence in the value 0.55, considering that uncertainty in the ICAP elemental analyses is 20% to 30% and that source elemental compositions (Table V) are even more uncertain.

Of greatest interest is the relative contribution of LAKE. As shown in Table VII, LAKE has a mean ratio of ~2, relative to CEMENT as well as to SOIL. This suggests that CEMENT and SOIL together just equal, on a total aerosol mass basis, LAKE. It is, however, important to note that the percent mass composition of Al, and even of Fe, is lower at the crib site than it was the previous year at midlake. The 0.4% mass for Al during the 1978 crib sampling is, in fact, one-fifth that in an elemental composition model for Chicago aerosol suggested by Gatz (1975). Thus, the SOIL contribution was anomalously low during crib sampling. The range in the ratio of LAKE to SOIL observed across the 18 filter sets is very wide, being anywhere from 0.5 to 4.8 for FINE and 0.3 to 4.6 for COARSE. Most of this variability is probably due to that in LAKE contribution to crib site aerosol mass and must be considered real since the total mean percent uncertainty for FINE LAKE is 55% and for COARSE LAKE 61%.

(These total uncertainties are the sum of the SOIL uncertainty and LAKE uncertainty since we are here considering a ratio of the two. The total mean percent uncertainty for CEMENT is 99% for FINE and 101% for COARSE.) The equally strong contribution of LAKE to fine and coarse aerosols over Lake Michigan (double that of SOIL) is surprising, especially considering the qualitative observation early in this discussion that fine/coarse fractions for the largely lake-derived Ca and Mg were reduced at the midlake site compared with the crib site. However, the fact that LAKE appears to be such a variable source suggests that the lake may be a strong local aerosol source. This latter point is in concert with the second qualitative observation that filter sets for no-lake-breeze conditions had significantly larger Ca and Mg EF's than the lake-breeze group of filter sets. The short overlake fetch of 3 to at most 10 km for the no-lake-breeze sets was apparently still sufficient to allow the lake to contribute Ca and Mg to the aerosol observed at the crib site so long as at least moderate windspeeds prevailed.

Separation into 8 lake-breeze and 10 no-lake-breeze filter sets results in the LAKE/SOIL ratios shown in Table VIII. The FINE LAKE mass contribution during lake-breeze occurrences is significantly below the overall ratio of two, whereas the ratio for FINE LAKE with no-lake-breeze (and short over-water fetch) is higher than this for most of the 10 sets in this group. There is no distinguishable difference for COARSE LAKE. The fact that windspeeds were 3.4 ± 1.5 m s^{-1} during lake-breeze sets and 6.0 ± 1.0 m s^{-1} during the short-fetch no-lake-breeze sets indicates that a local lake source can definitely contribute to crib site aerosol mass; Table VIII indicates a greater lake contribution in the fine fraction. The Table VIII data suggest that lake-derived fine ($d < 1$ μm) aerosol may be much more dependent upon mean windspeed, and that lake-derived coarse ($d > 1$ μm) aerosol may be omnipresent.

CONCLUSION

CEB analysis was successfully applied to the 68th Street crib site data base. Quantitative identification of a strong lake source (possibly local) aerosol supports qualitative indicators, based on Ca and Mg enrichment factors and fine/coarse aerosol fractions, that a lake source is significantly contributing to aerosol mass over Lake Michigan. This is true not only for coarse (diameter, $d > 1$ μm) aerosol but also for fine ($d < 1$ μm) aerosol. The lake source contribution to the fine aerosol mass is about equal to the sum of anthropogenic contributions (iron/steel manufacturing, oil burning and automobile exhaust). The strength of the fine aerosol lake source appears to be dependent upon mean windspeed whereas the coarse aerosol lake source appears to be much less so. The coarse aerosol lake source is very probably due to the jet drop generated during wave breaking whereas we may speculate that film drops are responsible for the fine aerosol lake source.

The lake source was found to contribute twice as much mass as did soil. This was so for both the fine and coarse fractions. However, the soil source appeared to contribute one-half to one-fifth less mass during the 1978 crib site field sampling effort than may be considered typical. If a four-times larger soil source contribution had been present, the lake source would have been found to contribute about half as much as the more typical soil source. Nonetheless, the lake as a source of aerosol mass must be carefully considered whenever aerosol data obtained over Lake Michigan, or any other of the Great Lakes, are being interpreted.

ACKNOWLEDGMENT

The authors wish to thank J. Forst, K. Walther, and W. Ward for tireless help with the field program; V. Jensen for his analytical assistance; Dixie Butz and Vera Rhimes for preparing the manuscript. We also wish to extend our appreciation to Tom Tisue of Argonne National Lab for the XRF analysis of our filter portions, and J. Schmidt for review of our manuscript draft. This work was supported by USEPA, Grant #R005301012.

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TABLE I

Element	Detection limit	Procedural blank	Typical sample
Al	90	290	2600
Ca	5000	5100	16400
Cd	2	6	120
Cu	9	40	230
Fe	120	240	6300
Mg	100	210	4900
Mn	6	20	500
Mo	6	30	75
Ni	5	40	75
Pb	45	80	4100
Sn	8	10	260
V	2	4	90
Zn	50	100	1800

Detection limits, procedural blanks, and typical sample concentrations for the ICAP method ($\mu g\ \ell^{-1}$)

TABLE II

Element	Mean Concentration of ICAP and XRF (ng m^{-3})	Mean Difference ICAP vs. XRF (%)
Fe	785	33
Mn	32	66
Ni	27	70
Pb	500	19
Zn	490	18

Results of ICAP and XRF analyses of 12 filter sets

TABLE III

Element	$\bar{C}$ nearshore, 1978 (ng m^{-3})	$\bar{C}$ midlake, 1977 (ng m^{-3})
Al	215	180
Ca	1340	770
Cd	10	n.d.
Cu	20	6
Fe	520	320
Mg	405	200
Mn	40	20
Mo	6	n.d.
Ni	6	n.d.
Pb	340	140
Sn	20	10
V	7	n.d.
Zn	150	55
P	20	35
N (NO_3)	3670	3100
S (SO_4)	5660	5100
Mass	57,600	31,800

Geometric mean concentrations of elements in aerosol at the 68th Street crib and midlake.

TABLE IV

Element	Nearshore EF	Nearshore Fine/Coarse Fraction	Nearshore % Mass Composition	Midlake EF	Midlake Fine/Coarse Fraction	Midlake % Mass Composition
Al	1.0	1.7	0.4	1.0	1.2	0.6
Ca	22	1.2	2.3	22	0.4	2.4
Cd	4300	15.6	<0.1			
Cu	190	5.5	<0.1	170	2.9	<0.1
Fe	4.6	3.3	0.9	3.5	1.6	1.0
Mg	26	2.2	0.7	23	0.6	0.6
Mn	11	3.1	<0.1	10	2.0	<0.1
Mo	580	5.8	<0.1			
Ni	230	7.2	<0.1			
Pb	5200	12.7	0.6	5200	17.3	0.4
Sn	690	4.7	<0.1			
V	100	7.4	<0.1			
Zn	580	4.4	0.3	530	6.1	0.2
P		7.6	<0.1		4.2	0.1
N (NO_3)		9.1	6.5		8.0	3.1
S (SO_4)		30.8	9.8		37.3	5.6

Comparison of parameterized characterizations of nearshore and midlake aerosols.

TABLE V

	Percent by Weight						
Element	LAKE	CEMENT	SOIL	COAL	STEEL	OIL	AUTO
Al	0.03±0.02	3.2±2.6	6.5±1.5	14±3	2.3±0.7	0.2±0.1	0.15±0.09
Ca	22±5	32±12	1.2±0.3	3.1±1.1	3.6±2.0	2.9±0.3	0.05±0.03
Cd	<0.01	<0.01	<0.01	0.01±0.01	<0.01	<0.01	<0.01
Cu	0.02±0.02	<0.01	<0.01	<0.01	1.4±0.6	0.09±0.06	<0.01
Fe	0.03±0.03	3.2±2.3	3.7±0.4	3.4±0.6	36±6	0.9±0.7	1.8±1.2
Mg	7.5±1.5	12±11	0.5±0.2	1.1±0.4	1.4±0.6	0.15±0.05	<0.01
Mn	0.01±0.01	0.1±0.1	0.08±0.04	0.04±0.02	2.5±0.5	0.02±0.01	<0.01
Pb	<0.01	<0.01	<0.01	0.01±0.01	<0.01	<0.01	25±5
V	<0.01	<0.01	0.01±0.01	0.03±0.02	<0.01	3.0±1.0	<0.01
Zn	0.02±0.02	0.03±0.02	<0.01	0.04±0.01	1.8±0.6	0.2±0.1	0.07±0.05
Na	2.1±0.4	<0.01	0.6±0.3	1.8±0.5	<0.01	1.6±0.8	<0.01
Ti	<0.01	<0.01	0.4±0.1	0.8±0.2	<0.01	<0.01	<0.01

Aerosol composition for various Chicago-region source types.

TABLE VI

Mean Ratio (Calculated to Observed)

Element	Using LAKE		Using CEMENT	
	Fine Fraction	Coarse Fraction	Fine Fraction	Coarse Fraction
Ca	1.24	0.86	0.88	0.87
Fe	1.0	1.01	1.04	1.04
Mg	0.85	0.78	0.68	0.82
Mn	0.93	0.95	0.98	0.94
Na	0.40	0.88	0.26	0.39
Zn	0.24	0.37	0.25	0.38

Ratio of CEB calculated (six-source linear combination) to observed elemental concentrations.

TABLE VII

Aerosol Fraction	Relative Weight (SOIL ≡ 1.0)					
	LAKE	CEMENT	STEEL	OIL	AUTO	COAL
FINE $(d < 1\ \mu m)$						
Mean Ratio	∿2	∿1	3/4	1/4	∿1	0.55
Range	0.5-4.8	0.2-2.8	0.3-1.5	0.1-0.5	0.2-2.5	0.4-0.7
COARSE $(d > 1\ \mu m)$						
Mean Ratio	∿2	>1	1/3	0	1/10	0
Range	0.3-4.6	0.2-3.3	0.1-0.6		0-0.2	

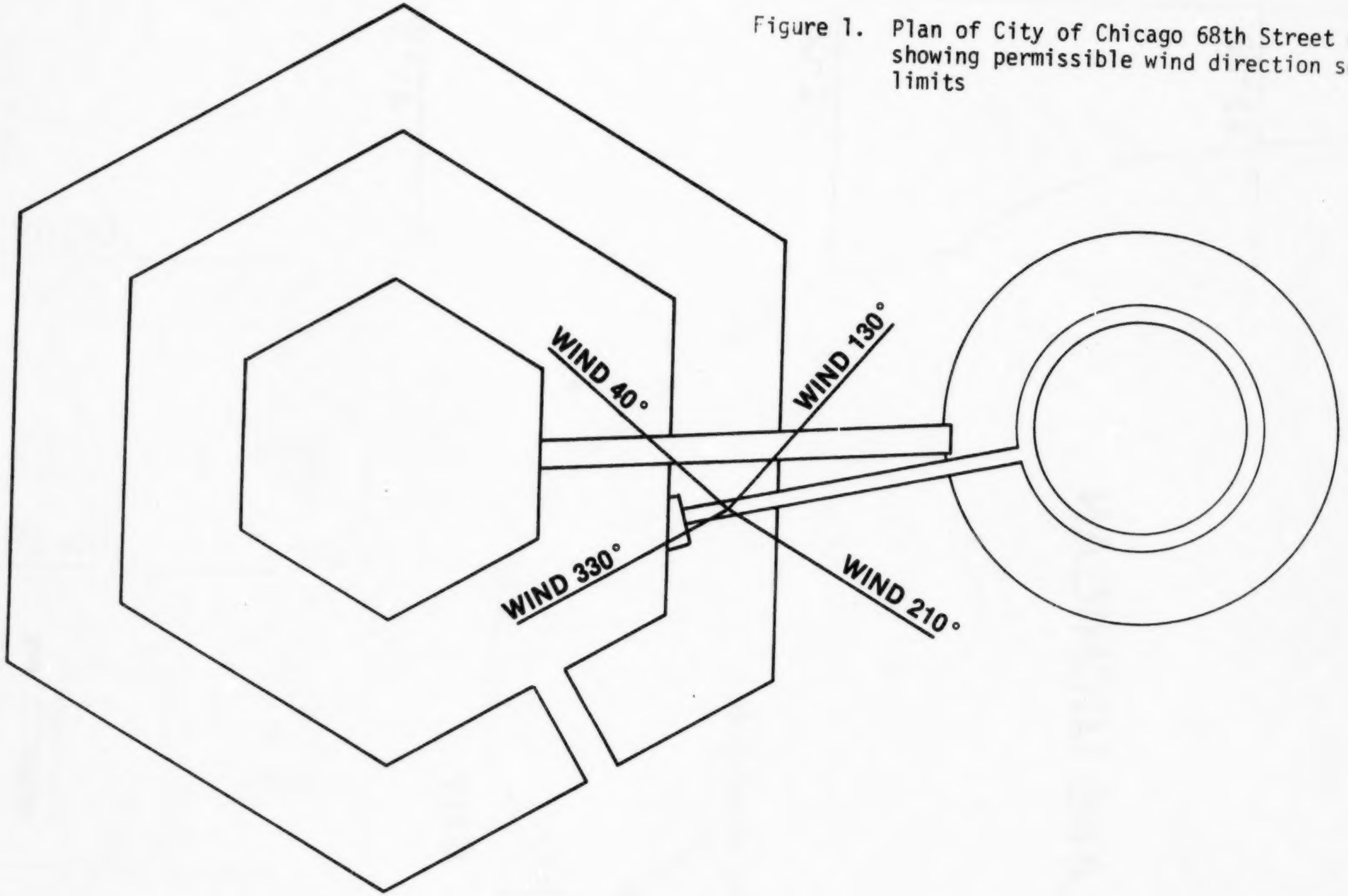
Relative weighting of six source types for fine and coarse aerosol fractions at the 68th Street crib site.

TABLE VIII

Aerosol Fraction \ Mean windspeed and fetch	Relative weight (SOIL ≡ 1.0)	
	3.4 ± 1.5 ms^{-1} LAKE with lake breeze (long over-water fetch)	6.0 ± 1.0 ms^{-1} LAKE with no lake breeze (short over-water fetch)
FINE (d < 1 μm)	1.0 ± 0.5	3.7 ± 2.2
COARSE (d > 1 μm)	2.4 ± 1.0	2.2 ± 2.1

Relative weighting of the lake source for fine and coarse aerosol fractions and as a function of fetch over the lake.

Figure 1. Plan of City of Chicago 68th Street crib, showing permissible wind direction sector limits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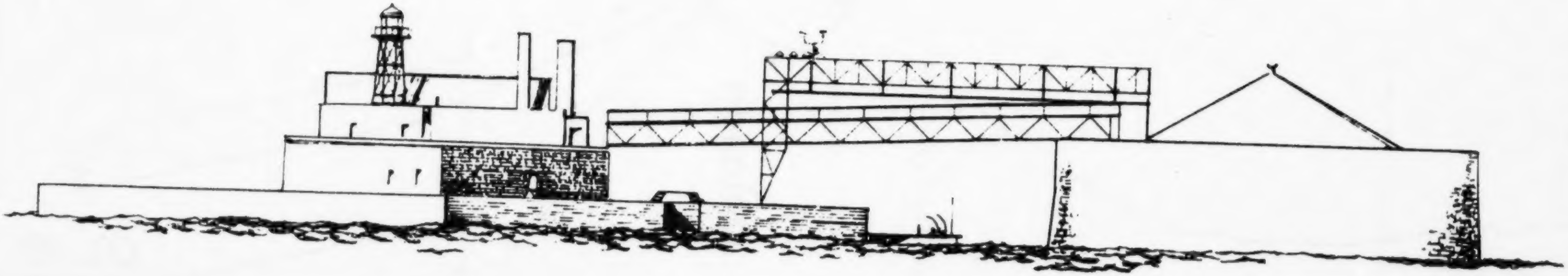
WIND 130°
WIND 330°
WIND 210°



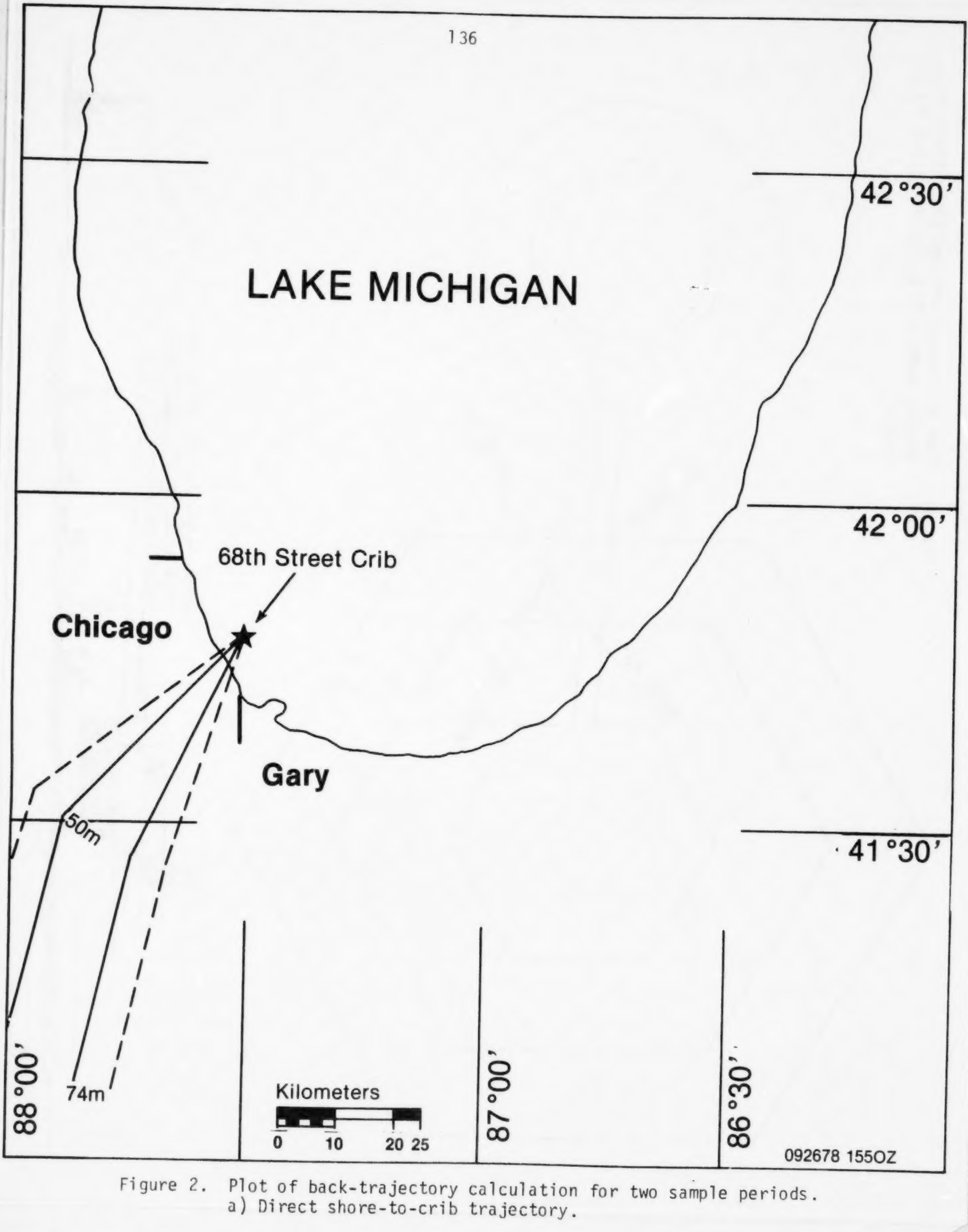

42°30'
LAKE MICHIGAN
42°00'
68th Street Crib
Chicago
Gary
50m
41°30'
74m
88°00'
87°00'
86°30'
Kilometers
0
10
20
25
092678 1550Z

Figure 2. Plot of back-trajectory calculation for two sample periods.
a) Direct shore-to-crib trajectory.

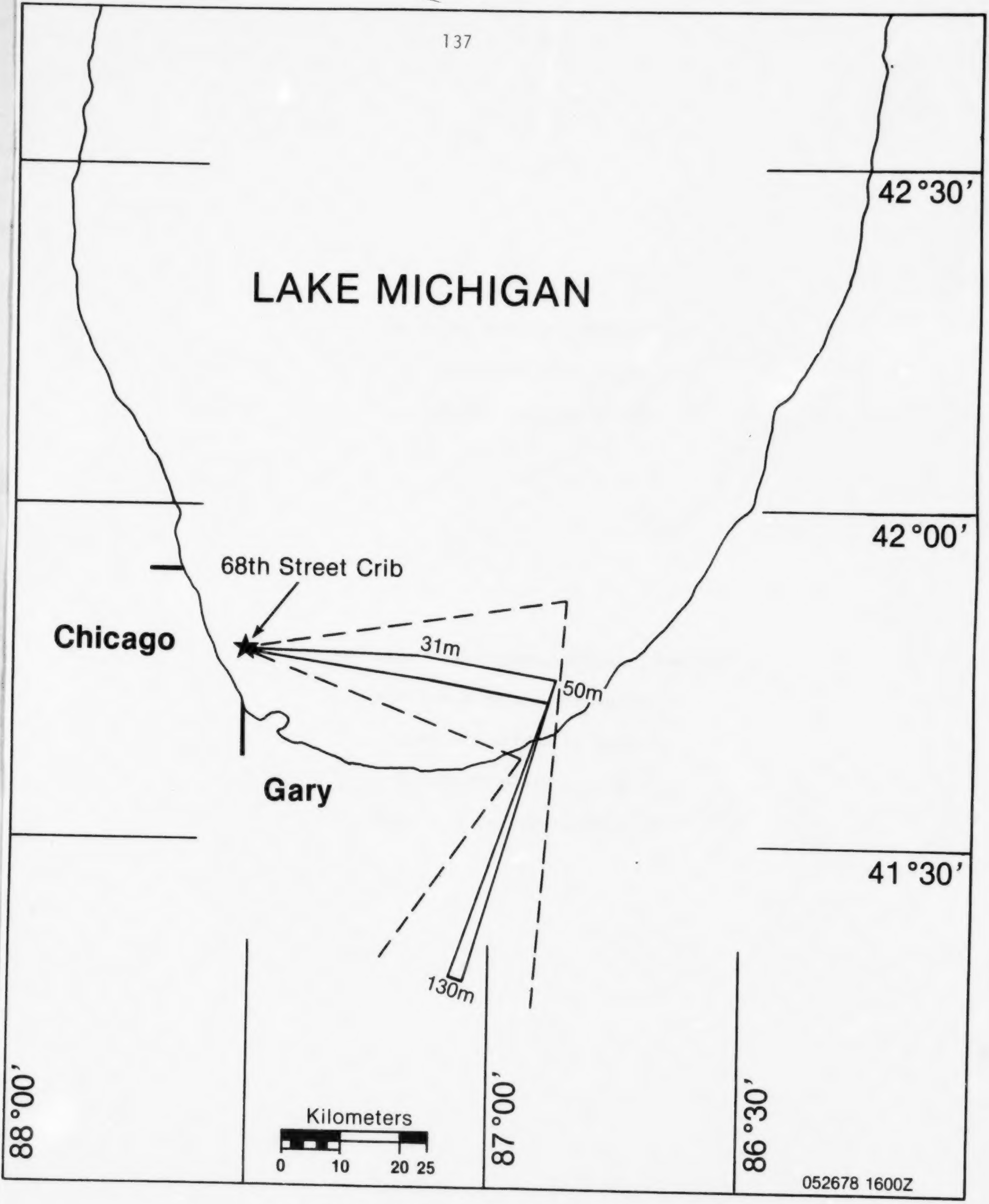

LAKE MICHIGAN
42°30'
42°00'
41°30'
68th Street Crib
Chicago
Gary
31m
50m
130m
88°00'
87°00'
86°30'
Kilometers
0
10
20
25
052678 1600Z

Figure 2 b) Trajectory influenced by lake breeze event.

APPENDIX E

SOME EFFECTS OF WIND-SHIFT ON OVER-LAKE TURBULENCE AND AEROSOL DEPOSITION

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Abstract

Aircraft measurements of turbulence spectra and surface measurements of total aerosol mass derived from size distributions were compared for periods with and without windshift over the southern basin of Lake Michigan in September of 1977 and May of 1978. It was found that wind shifts are associated with depletion of near-surface aerosol mass and with departures from isotropy in the inertial subrange as indicated by difference of the ratio of vertical velocity spectra to longitudinal velocity spectra from the isotropic value of 4/3. Velocity spectra were measured by fixed and rotating vanes mounted on the aircraft nose boom. Aerosol size distributions were measured by a laser scattering particle counter.

I. Introduction

Dry deposition of atmospheric aerosols to water bodies has, within the last decade, come to be recognized as an important and, for some substances, predominant route for the influx of matter. Winchester and Nifong (1971) calculated atmospheric loading rates for the region of the southern basin of Lake Michigan. This model has been variously modified by Skibin (1973), Sievering (1976) and others. These studies and those by Gatz (1975a and 1975b) not only found increased estimated loadings to the lake by the atmospheric route, but pointed out large uncertainties in these estimates, stemming from a lack of understanding of the boundary layer dynamics of aerosols and lack of *in situ* measurements of dry deposition over the lake.

The most direct method of measuring aerosol flux, the eddy correlation method, has proved to be unwieldy in the field and especially on a lake surface (Williams *et al.*, 1980). There has been enough evidence, however, to note a large discrepancy between measurements done in a wind tunnel (Sehmel and Sutter, 1974) and those taker under field conditions. Construction of a model capable of accurately predicting deposition of aerosols to a water surface requires consideration of all phenomena contributing to this discrepancy. Several explanations have been proposed in the literature (see review article by Slinn *et al.*, 1978). One possible phenomenon discussed by Slinn (1979) is the rapid uptake of water vapor by aerosols in the high humidity environment near the surface and subsequent gravitational fallout.

Another mechanism suggested by Sievering (1980) involves direct impaction of particles on those elements of the surface which protrude through the laminar sub-layer. When a continuous laminar sub-layer is present, one may expect more than an order of magnitude variation in aerosol deposition for the $0.1 < d < 2$ μm size range. It was found experimentally (Sievering, 1980) that a two-to three-fold variation prevailed in this size range under conditions of moderate wind speed (2.4 to 8.2 m sec^{-1}). If these experimental data are truly representative of air/water aerosol exchange for moderate wind-speed regimes, then non-steady state conditions must predominate above the interface. That is, turbulence-induced eddies may advect aerosols to surface roughness elements protruding outside a possibly discontinuous sublayer resulting in direct impaction.

One of the ways in which deposition to a water surface differs from deposition to land or vegetation is that a water body adapts its surface characteristics to the wind. There is, particularly over large bodies of water, a lag between a change in the wind regime and the adaptation of the wave train (SethuRaman, 1978). During this period of maladjustment, elements of the water surface are most prone to protrusion through the laminar sublayer. A change in wind speed or direction perturbs the equilibrium between a water surface and a steady-state wind, and would be expected to also perturb the state of isotropy which is presumed to occur within the inertial subrange of the momentum power spectrum in the absence of unusual sources or sinks of kinetic energy. One necessary, but not sufficient, indicator of the presence of an isotropic state is the ratio of the vertical velocity (or lateral velocity) spectrum to the longitudinal velocity spectrum. In the inertial subrange, this ratio is thought to approach the value 4/3 under isotropic conditions. Departures from this value in over-water environments relative to over-land environments have been previously noted using a variety of measurement techniques (Schmitt, Friehe and Gibson, 1978).

2. Instrumentation

Turbulence measurements were taken aboard a Beechcraft *Queenaire* aircraft provided by the Research Aviation Facility of the National Center for Atmospheric Research. The aircraft departed from Midway airport and upon reaching the lake proceeded at a low altitude (usually 30 m) to the midlake sampling site 87°00'W, 42° 00'N (see fig. 1). Vertical soundings were taken in a square spiral "box" pattern over this site, over a point halfway to shore 87°15'W, 41°55'N (referred to as the "halfway point") and over a nearshore sampling site, a City of Chicago water intake crib 87°32 'W, 41°37'N. Soundings extended from about 15 m through about 1800m. Flight times were approximately 0700-0900, 1100-1400 and occasionally 1600-1800 Central Daylight Time (CDT) during September 26-30 of 1977 and May 17-19, 22, and 24-26 of 1978.

Constrained and rotating vanes mounted on a nose boom of the aircraft (Lenschow, 1971) were used to measure velocity. Also on the aircraft were fast-response pressure, temperature and humidity sensors. These data were recorded at a rate of 10 hz by an on-board data system (Glaser, 1973).

Concurrently with the aircraft data, meteorological and aerosol data were gathered at the surface. During September of 1977, the data were collected aboard the R/V *Simons* at the midlake sampling site

During May 1978, the surface sampling site was the water intake crib

Among other analyses of the surface data, trajectories of the air parcels sampled were calculated backwards in time. The sampling site wind vector was used for this trajectory as long as the parcel had not penetrated the surface layer which was assumed to be at a height of 50 m. The vertical velocity of the parcel was estimated by a momentum-analogue deposition velocity calculated from the windspeed at 5m and the temperature stability. After penetration of the surface layer, the wind vector was calculated from a weighted average of the surface data and a triangulation average of National Weater Service upper level soundings. The process is more fully described in Sievering et al. (1979). The trajectories, though they had large uncertainties, were sufficiently accurate to provide an indication of the source regions of the air sampled and a means of calculating the degree of windshift.

An Active Scattering Aerosol Spectrometer (ASAS), which counted particles in each of 60 size channels in the range $0.23 < d < 30.0$ μm for September data collection and $0.11 < d < 3.5$ μm in May by scattering of a He-Ne laser source (see Schuster and Knollenberg, 1972), was mounted on board the aircraft. During May 1978 a second ASAS was operated at the lake surface. ASAS data obtained during 1977 was collected at the midlake site. Several instrument-related problems make the validity of absolute numbers suspect, but comparisons between periods of ASAS operation should be realistic. Integration of the aerosol size spectra multiplied by $4/3 \pi r^3$ and an assumed particle density of 2 g cm^{-3} yields a measurement of total aerosol mass per volume of air sampled assuming sphericity of particles and uniform density. An integrating nephelomter (IN) allowed independent verification of mass measurements (see Dave, Dolske, and Sievering, 1979).

3. Analysis

The 10 hz values of the three velocity components were analyzed by a fast-Fourier transform method and the resultant spectra were plotted. In addition, the ratio of vertical to longitudinal velocity (S_w/S_u) was calculated in the wavelength range $10 < \lambda < 300$m which was presumed to lie within the inertial subrange.

In an attempt to find a relationship between the degree of variability in wind direction and the departure from isotropy, a "windshiftiness" parameter was developed. This parameter estimates the persistence of any one wind direction as the ratio of path length to displacement or s/ℓ, where s is the trajectory path length and ℓ is the straight-line displacement of a parcel from start to end of trajectory. This parameter is unity for perfectly straight flow and unbounded above for convoluted trajectories. A total of eleven flights occurred concurrently with surface sampling during September of 1977 and May of 1978. Of these, two could not be used because of faulty data (see Table 1). When a rank correlation was done between the "windshiftiness" parameter and $\left|4/3 - S_w S_u\right|$, the rank correlation coefficient was 0.925 (see Table 2) allowing one to reject the hypothesis of zero correlation at better than the one percent level.

Comparison of aerosol mass measurements with wind direction shifts is another method of investigating the relationship between windshift and near-surface effects. It elucidates turbulence behavior less directly, but still involves a direct measurement of atmospheric aerosols. A case study of midlake sampling site data for the period from 18 May 1977 to 19 May 1977 is particularly relevant. Table 3 lists six periods over which data were collected, and certain associated meteorological and aerosol measurements. In this table, stability (ΔT) is the air temperature measured at a height of 5 m minus the surface temperature (measured by infrared thermometry). The wind speed and wind direction were also measured at 5m. All values are averages of measurements taken every fifteen minutes across the period indicated. The mass, calculated by integration of the aerosol size spectra, allows one to discriminate between mass due to fine particles $(0.11 < d < 1\ \mu m)$ and an estimated total measured was by the IN (approximately $0.1 < d < 1.0$)

or the ASAS ($0.11 < d \leq 3.5$ μm).

An abrupt windshift from 240° to 170° took place between 1230 and 1300 CDT on 18 May 1977, i.e., near the start of data set 20080. Before this period the southern basin of Lake Michigan had been under west-south-westerly winds for over 10 hours. As a result the midlake area and, presumably, points south and southwest were under the influence of the Chicago plume, as evidenced by the high mass measurements for data sets 20060 and 20070. After the windshift, it should have taken about 4½ hours for the slightly less polluted south-shore plume, traveling at the mean wind velocity of 1.9 m $\sec^{-1}$, to reach the sampling site. Thus, only the last 20% of data set 20080 should have been sampling south shore air. Yet, in spite of continued strong stability and light wind speeds, there is a sixfold drop in aerosol mass. The large standard deviation in the wind direction for data sets 20080 and 20090 resulted from the fact that during this period, the wind direction swung from 180° to 100° and back again.

There is another abrupt windshift and, perhaps more important, a severe decrease in the standard deviation on wind direction, between 2100 and 2200 on 18 May 1977. A parcel which left shore at this time would reach the sampling site just about the time the heavily-loaded data set 20110 was begun. In summary, the indication is that the period of continuous windshift is associated with a severe decrease in total aerosol mass near the surface.

4. Summary and Conclusions

The ratio of vertical to longitudinal velocity in the inertial subrange was measured by aircraft over Lake Michigan. When near surface values of this ratio were compared to an estimator of the degree of windshift, a correlation was found suggesting that "windshiftiness" over Lake Michigan is associated with departures from isotropy, as would be expected if increased wind shifts induced protrusions of roughness elements through the laminar sub-layer.

A case study was presented in which wind shifts are followed by a decrease in aerosol mass concentration, consistent with the hypothesis that increases in the protrusion of roughness elements will promote direct impaction of aerosols on the water surface.

6. Acknowledgements

Appreciation is extended to the personnel of the Research Aviation Facility (especially P. Spyers-Duran) and the Computing Facility of the National Center for Atmospheric Research. The plotting of trajectories was performed by Vic Jensen and Patric McCoy. Gratitude is expressed to Brenda Chapman for preparation of the manuscript.

This work was supported by the U.S. Environmental Protection Agency under contracts R00530101 and R00542101.

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Table Captions

1. Various meterological parameters measured over Lake Michigan during September 1977 and May 1978.

2. Rank of "windshiftiness" parameter and $|4/3 - S_w/S_u|$ measured over Lake Michigan during September 1977 and May 1978.

3. Sample time meteorological parameters and aerosol data measured over Lake Michigan during May of 1977.

TABLE 1

Date	Time (CDT)	Average Wind Direction	Average Wind Speed (m $\sec^{-1}$)	Wind-shiftiness Parameter
26 Sept.	1641 - 1810	265	6.0	1.0
17 Sept.	0639 - 0919	319	7.4	1.03
27 Sept.	1109 - 1344	300	6.5	1.01
27 Sept.	1636 - 1823	295	6.1	1.01
17 May	0650 - 1810	4	3.5	1.07
18 May	1130 - 1256	69	3.0	1.11
19 May	1145 - 1330	91	3.5	1.004
24 May	1130 - 1420	25	1.4	1.08
25 May	1145 - 1447	90	5.7	1.42

TABLE 2

Date	Time (CDT)	Rank of Wind-Shiftiness	Rank of $\lvert 4/3 - S_w/S_u \rvert$
27 Sept	1641 - 1810	9	8
27 Sept	0639 - 0919	5	5
27 Sept	1109 - 1344	6.5	7
27 Sept	1636 - 1823	6.5	6
17 May	0650 - 0810	4	2.5
18 May	1130 - 1256	2	1
19 May	1145 - 1330	8	9
24 May	1130 - 1420	3	4
25 May	1145 - 1447	1	2.5

14.

			Meteorology			Aerosol Mass ($\mu g/m^3$)	
		$\overline{\Delta T}$	$\overline{u}(5)$	$\overline{WD}$	IN-derived Mass	ASAS dervied Mass	
Data Set	Time (CDT)	(^oC)	(m/s)	(^{o})		< 1.0 μm	Total
20060	5/18 03:00-5/18 06:00	5.9 ± 1.4	4.5 ± 0.2	240 ± 10	125	160	169
20070	5/18 08:20-5/18 11:20	6.7 ± 3.6	3.6 ± 0.3	239 ± 8	266	174	193
20080	5/18 12:00-5/18 17:25	9.5 ± 3.5	1.9 ± 0.6	174 ± 46	141	29	31
20090	5/18 17:45-5/18 21:00	11:4 ± 3.7	3.8 ± 0.3	140 ± 40	110	29	34
20100	5/18 22:00-5/19 01:30	13.3 ± 2.1	3.7 ± 0.9	212 ± 8	47	19	23
20110	5/19 01:45-5/19 06:15	7.2 ± 2.9	2.7 ± 0.4	212 ± 26	141	133	333

Table 3. Sample Time, Meteorological Parameters, and Aerosol Data Measured over Lake Michigan during May of 1977

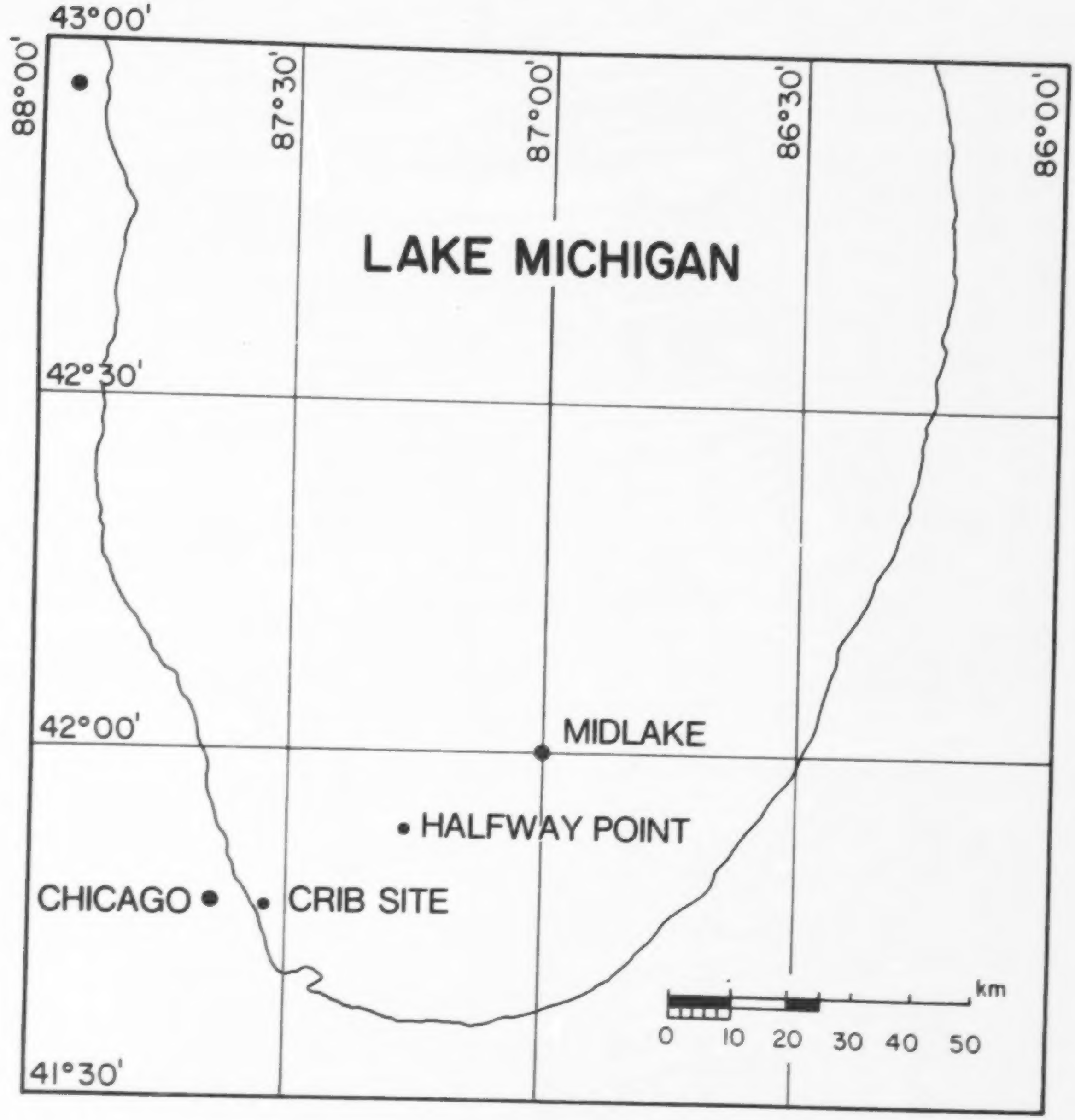
43°00'
88°00'
87°30'
87°00'
86°30'
86°00'
LAKE MICHIGAN
42°30'
42°00'
MIDLAKE
HALFWAY POINT
CHICAGO
CRIB SITE
km
0
10
20
30
40
50
41°30'

Figure 1. Location of Sampling Sites.